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DECOMPOSITION OF
NITRATE ESTERS

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A Phase 1 Final Report submitted to

Naval Surface Warfare Center
Indian Head Division
Indian Head, MD

for the

**ULTRA-VIOLET / ELECTRON BEAM DETOXIFICATION OF
NITROGLYCERIN / PROPYLENE GLYCOL DINRATE
WASTE WATER**

Contract N00174-92-C-0121

submitted by

DAMILIC Corporation
6290 Montrose Road
Rockville, MD 20852

March 16, 1994

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A Phase I Final Report for the
UV/EB DETOXIFICATION OF NG/PGDN WASTE WATER

submitted by

DAMILIC Corporation
6290 Montrose Road
Rockville, MD 20852

1.0 SUMMARY

The principal objective of this two year program is to develop an industrial radiation process for the destruction of the explosive nitrate ester compounds in several production waste water streams at the Navy's facilities in Indian Head, Maryland. Using Fourier Transform Infrared (FTIR), electrospray-mass spectroscopy (MS), and GC-MS, UV and EB treated waste water streams were evaluated for post treatment non-volatile content. The results confirm that:

1. UV and EB processing of nitroglycerine contaminated waste water (1) reduced the original organic nitrates to less than 1 ppm, and (2) converted more than 98.5% of the original nitrate esters to glycerine. Concomitant with the cleavage of the nitrate groups from the nitrate esters was the production of nitric acid and a reduction of the solution's pH from >7 to 2. A summary of the non-volatile organic byproducts produced by UV and EB treatment of the wastewater, and their relative values, is shown in Table I.
2. Based on the dose requirement to reduce the NG level less than 1 ppm, installation costs for and EB treatment system for the Biazzi Plant are estimated to be less than \$900,000.00. Operating costs are estimated to be less than \$50/1000 USG.
3. No qualitative or quantitative difference between UV and EB treated samples were observed for comparably treated samples.

2.0 INTRODUCTION

2.1 Background

The U.S. Defense Department in general, and the Indian Head Division of the Naval Surface Warfare Center in particular, manufacture a broad range of energetic materials for use as weapons, propellants, and specialty explosives (e.g. aircraft ejection charges). Although the manufacturing process is well characterized, designed, and carefully controlled to maximize safety and minimize waste, both energetic and toxic materials can be found in production waste water. Compounds commonly found in waste streams include nitroglycerine, propylene glycol dinitrate (PGDN), trimethylolethane trinitrate (TMETN), and triethylene glycol dinitrate (TEGDN). Although measurable, the concentrations of these materials in the waste stream have historically been low enough to satisfy the Environmental Protection Agency while incurring minimal disposal costs.

Recently, environmental concerns regarding manufacturing waste streams have forced a reevaluation by the Defense Department of its production facilities. The problem has, for facilities such as Indian Head, been exacerbated by the encroachment of the local population.

The Navy and others are currently evaluating a range of technologies to destroy and/or detoxify the waste streams of various energetic material production facilities. These include

Table I: NG DECOMPOSITION BYPRODUCTS IN TRANSFER WATER (Reported as a weight percentage of the organic constituents remaining in solution following treatment)

Primary UV and EB Decomposition Byproducts	
Byproduct	%
Organic	
Glycerine	98.5
Dinitroglycerine	< MDL
Mononitroglycerine	< MDL
Methanol	< MDL
Ethyl dinitrate	< MDL
Ethyl nitrate	< MDL
Methyl nitrate	< MDL
Formaldehyde	< MDL
Formic acid	< MDL
Oxalic acid	< MDL
Glyoxylic acid	< MDL
Glycollic acid	< MDL
Inorganic Nitrates	> 90

MDL = Minimum Detectable Level (0.1%)

filter, ultraviolet, and chemical techniques. This project extends the Navy's understanding of the byproducts produced by the UV and EB clean-up of these waste streams.

2.2 Ionizing Radiation from Electron Accelerators:

It is essential to recognize three aspects of electron irradiation processing:

1. Radioactivity is not involved in any way whatever. Neither the irradiated waste stream, nor the radiation vault, nor the accelerator itself become radioactive. The radiation field goes on when the accelerator is turned on; it vanishes immediately after it is turned off. There is absolutely no hazard to the community. Hazard to operating personnel are no different from those faced by workers in a medical radiation therapy center.
2. The devices considered for use in this application are off-the-shelf accelerators that operate in industrial settings on a round-the-clock basis with better than 98% availability. Some 800 are used in industry, almost all operated by semi-skilled personnel.
3. The size of the equipment is relatively small. A 5,000 ft² building, perhaps 20 feet high, is adequate to house the radiation vault, the accelerator, and the materials handling equipment.

2.3 The Effect of Electron Irradiation:

The principal effect of electron treatment of aqueous solutions is to produce, in good yield, several reactive intermediates -- both oxidizing (the hydroxyl radical) and reducing (the hydrated electron and the hydrogen atom). It is the transient redox species and their reactions with water impurities that form the basis for this approach. The reason is that the rate constants with the nitrate ester solutes of interest are very high. The addition of ozone and H₂O₂ are certain to provide an enhancement effect.

The reason for the confidence in the net effects expected is the fact that radiation treatment of industrial waste streams has been a matter of considerable study in the past. A few supporting literature citations are referenced.

Another basis for the confidence is the fact that studies performed at the Naval Surface Warfare Center, Indian Head Division have demonstrated that ultraviolet light (UV) destroys nitrate esters; both ozone and H_2O_2 combined with pH adjustment enhance the reaction.

2.4 OH-induced reactions

OH radicals are effective oxidizing species that can abstract hydrogen from nitro-ester molecules. These abstraction reactions produce free radicals at rates, in general, near the diffusion-controlled limit. Once the abstraction reaction has produced a free radical on a nitrate ester, subsequent reactions with dissolved oxygen and other OH radicals can swiftly lead to alcohols and inorganic nitrate. Hydrolysis of the radical leading to cleavage of the nitrate is another rapid reaction.

2.5 e^-_{aq} & H atoms-induced reactions

Solvated electrons and H-atoms are reducing species. They also react with nitro-ester compounds at diffusion controlled reactions rates. Just like OH radicals, their reaction with the polymer can produce free radicals that undergo various types of degradation reactions. For example, the reaction of solvated electrons e^-_{aq} can cause the nitrate groups to be released.

The dissolved oxygen is an effective competitor converting e^-_{aq} to $\text{O}_2^{\cdot-}$ which leads to the OH based reactions described above. The reaction of H atoms with nitrate esters can also lead indirectly to partial cleavage. The mechanism is expected to be similar to that of OH radicals since both undergo initial hydrogen abstraction reactions.

2.6 Oxygen Effects

Dissolved oxygen in water plays a major role in the radiation chemistry of organic compounds. In general, radiolytically produced organic free radicals react very fast with the dissolved oxygen in water to produce peroxy radicals. Peroxy radicals are powerful oxidizing species that can, through a series of reactions, destroy nitro-ester molecules. The nature of these reactions depends on the organic peroxide's molecular structure, the oxygen concentration, the pH of the aqueous medium, and the dose-rate. In addition, the other primary radicals generated in the radiolysis of water (i.e. the H-atoms and the hydrated electron e^-_{aq}) also react with O_2 .

3.0 WATER SAMPLES

All measurements were performed on waste water samples prepared by Indian Head and supplied to DAMILIC Corporation. In accordance with instructions supplied by NSWC, Indian Head Division, some samples were modified by the addition of salts to simulate actual waste streams. Some samples were then treated by Solarchem Environmental by a proprietary UV process and others were treated by DAMILIC Corporation with high energy electrons (EB). The initial NG and PGDN concentrations and pH values for the waste streams are summarized in Table II.

4.0 PHOTOINDUCED DECOMPOSITION IN THE PRESENCE OF H_2O_2

4.1 Introduction

Waste water was irradiated with UV light in the presence of hydrogen peroxide at Solarchem Environmental Systems (Richmond Hill, Ontario) and previously reported (Indian Head Contract No. N00174-90-C-0068). No details were made available to us concerning the Solarchem UV source (e.g. intensity, H_2O_2 , and wavelength).

The resultant decomposition products of the Solarchem processes were then analyzed by electrospray mass spectrometry, gas chromatography-mass spectrometry, and infrared spectroscopy. These are shown in Table I.

Table II: CONCENTRATION AND pH MEASUREMENT OF PGDN AND NG IN ACTUAL WASTE STREAMS

Organic nitrate	Type of waste water	Concentration (ppm)	pH ^d	Comments
PGDN	Transfer water	1580 ^a	8.42	Provided by Navy from Catch Tank "B"
PGDN	Wash water	1100 ^a	7.53	Provided by Navy from Catch TK ₁
NG	Transfer water	940	5.34	Provided by Navy
NG	Wash water	1200 ^b 660 ^c	9.75	Provided by Navy and 1% CO ₃ ⁻² , 1% HCO ₃ ⁻ , 3% NO ₃ ⁻ and 2% SO ₄ ⁻² were added at UMCP on 5/17/1993.

Notes:

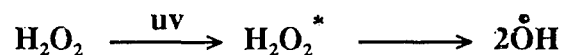
1. ^a---Measured at UMCP on 5/27/1993.
2. ^b---NG concentration before salts were added.
3. ^c---Measured on 5/27/1993, 10 days after addition of the salts(hydrolysis).
4. ^d---Measured on 5/17/1993.

4.2 Primary Reactions

In our analysis of the mechanism, there are two primary reactions in the Solarchem process.

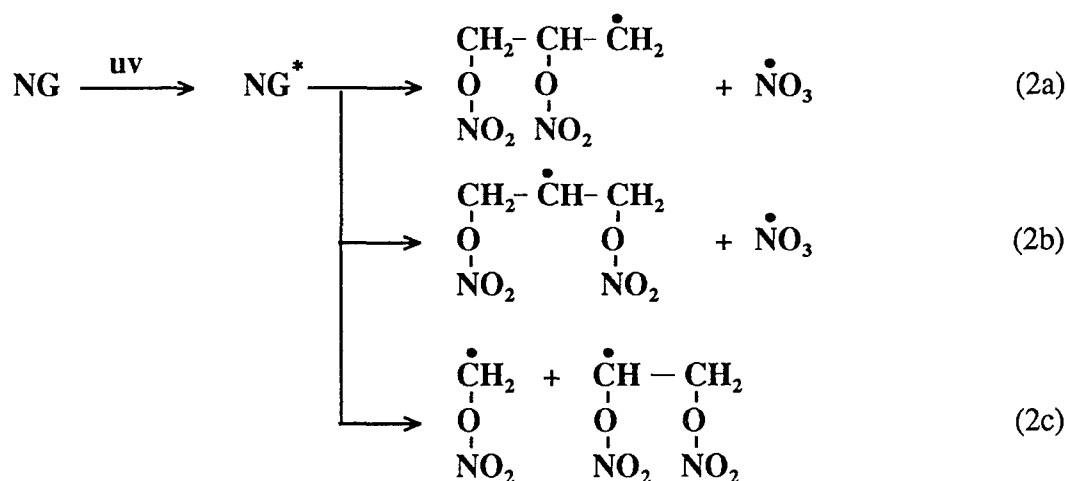
The first is the decomposition of the hydrogen peroxide into the hydroxyl radical:

(1)



A second reaction is the direct absorption of the UV light by the principal chromophore -- the nitrate group on the nitrate ester. The absorption by the nitrate group causes the excitation of the molecule and the ejection of a nitrate radical:

(2)



The dissociated nitrate radical may be from the terminal (2a) or pendant (2b) position, thus leaving behind either a primary or secondary alkyl free radical that can undergo further reactions. One such reaction is the creation of a dimer through the combination of two such radicals. This species was observed by us as a major byproduct in all GC analyzed samples (see Figure 1, Gas Chromatograph of UV treated NG sample). Data to date strongly suggests however, that the dimers are a product of the GC analysis alone. The 4.36 min. GC peak (scan 167) produced MS products of 166 and 151 m/z corresponding to the dimer of glycerol following the loss of OH and CH₂ groups during the MS analysis. No significant dimer production was observed from UV or EB processing.

An additional reaction that can result from the excitation of the nitrate group, is the direct break of a carbon-carbon bond (2c). As with the dinitroglycerine radical, these two free radicals must ultimately react to form dimers or further degrade. Although not evaluated in this study, previous work by Hempfling (IHTR 1427) showed, but did not identify low molecular weight degradation fragments in partially treated UV samples. These byproducts are almost certainly derived from the methylnitrate and ethyl dinitrate species shown in equation (2). Their reactions are described in greater detail below (pp. 12 - 15).

The nitrate radical that is produced in equation (2) is also important. This radical will react with water to produce nitric acid and a hydroxyl radical:

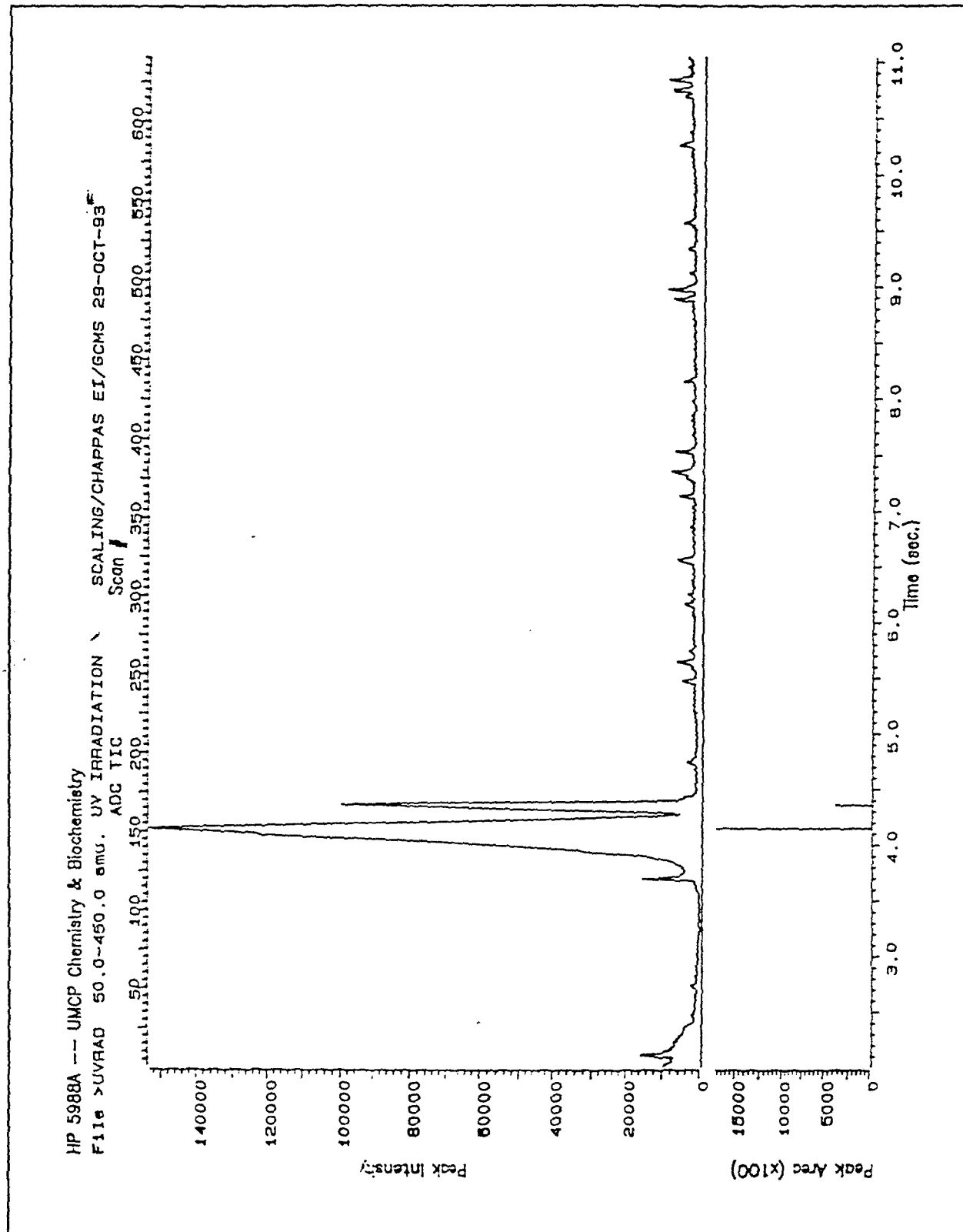


Figure 1: Gas Chromatograph of UV treated NG sample

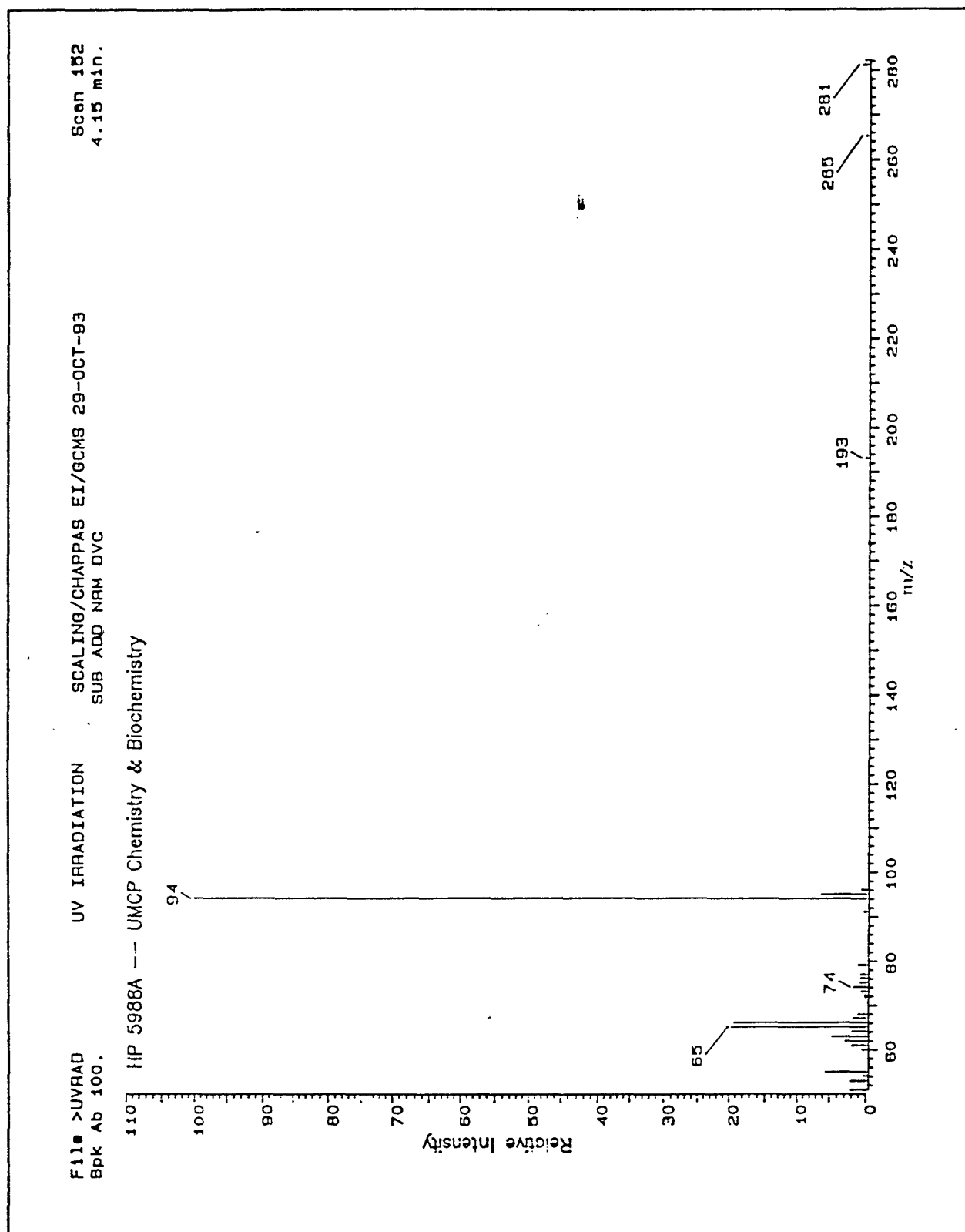


Figure 2: Mass Spectrum of UV treated NG sample, Scan 152

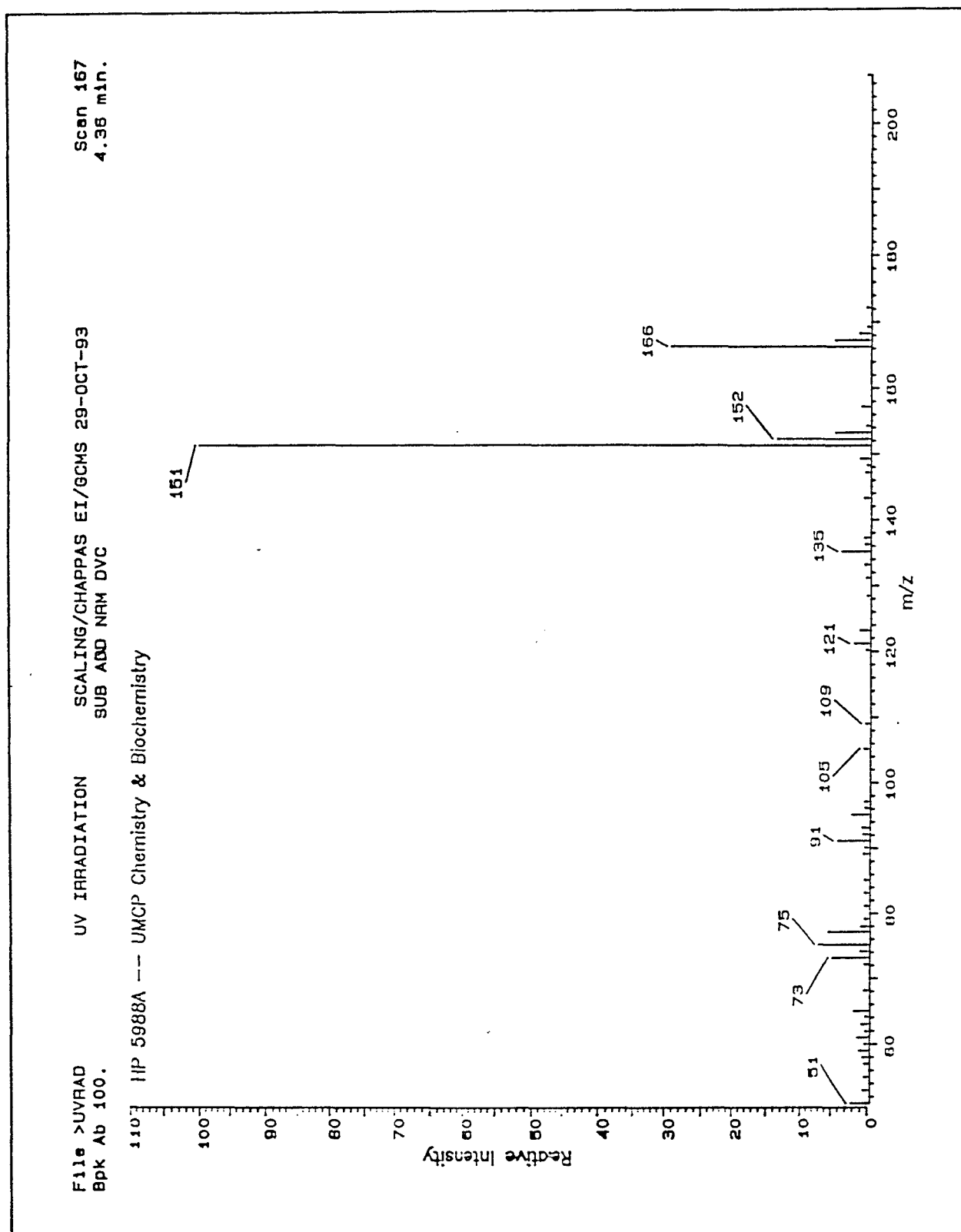


Figure 3: Mass Spectrum of UV treated NG sample, Scan 167

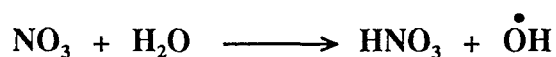
Table III: pH FOR UV AND ELECTRON BEAM IRRADIATED NG AND PGDN SAMPLES

Sample ID	Before any treatment	UV-treated			100kGy electron beam irradiated
	Measuring date	Measuring date			Measuring date
	7/22	7/14	7/15	7/22	7/22 ^b
NG ww	9.41	9.40 ^a	9.39	9.39	9.41
NG tw	9.01---→5.38 ^c	1.95 ^a	1.95	1.95	2.19
PGDN ww	8.76	6.19 ^a	6.15	6.15	3.06
PGDN tw	8.30---→7.62 ^c	1.87 ^a	1.86	1.87	2.34

Notes:

1. Tw,ww---Transfer and wash water respectively.
2. ^a---The UV-treatment dates are as follows: 7/9 for NG tw and 7/12 for all other three samples.
3. ^b---The electron beam irradiation date is 7/22.
4. ^c---For both transfer waters, their original pH values were unstable, going down continuously from the initial values to the final values respectively without stirring during pH measurement.

(3)

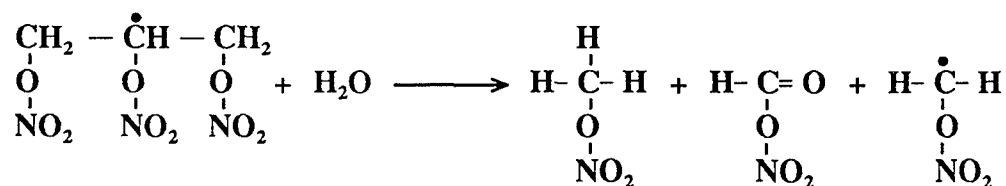


This reaction is consistent with the drop in pH (see Table III) of the solution during irradiation. This hydroxyl radical, just like the hydroxyl radicals produced by the dissociation

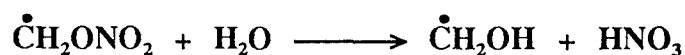
of the hydrogen peroxide, plays a major role in the degradation of the organic materials in the water.

The methyl, ethyl, and propyl nitrate ester radicals follow one of two reaction paths: (a) hydrolysis resulting in the ultimate conversion of the organic nitrate to methanol, formaldehyde, and glycol (4,5,6) or (b) reactions with oxygen to produce carbon dioxide, formic acid, and oxalic acid (19).

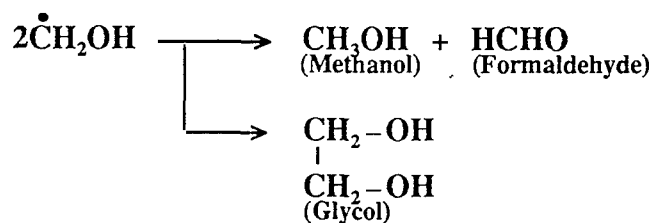
(4)



(5)



(6)



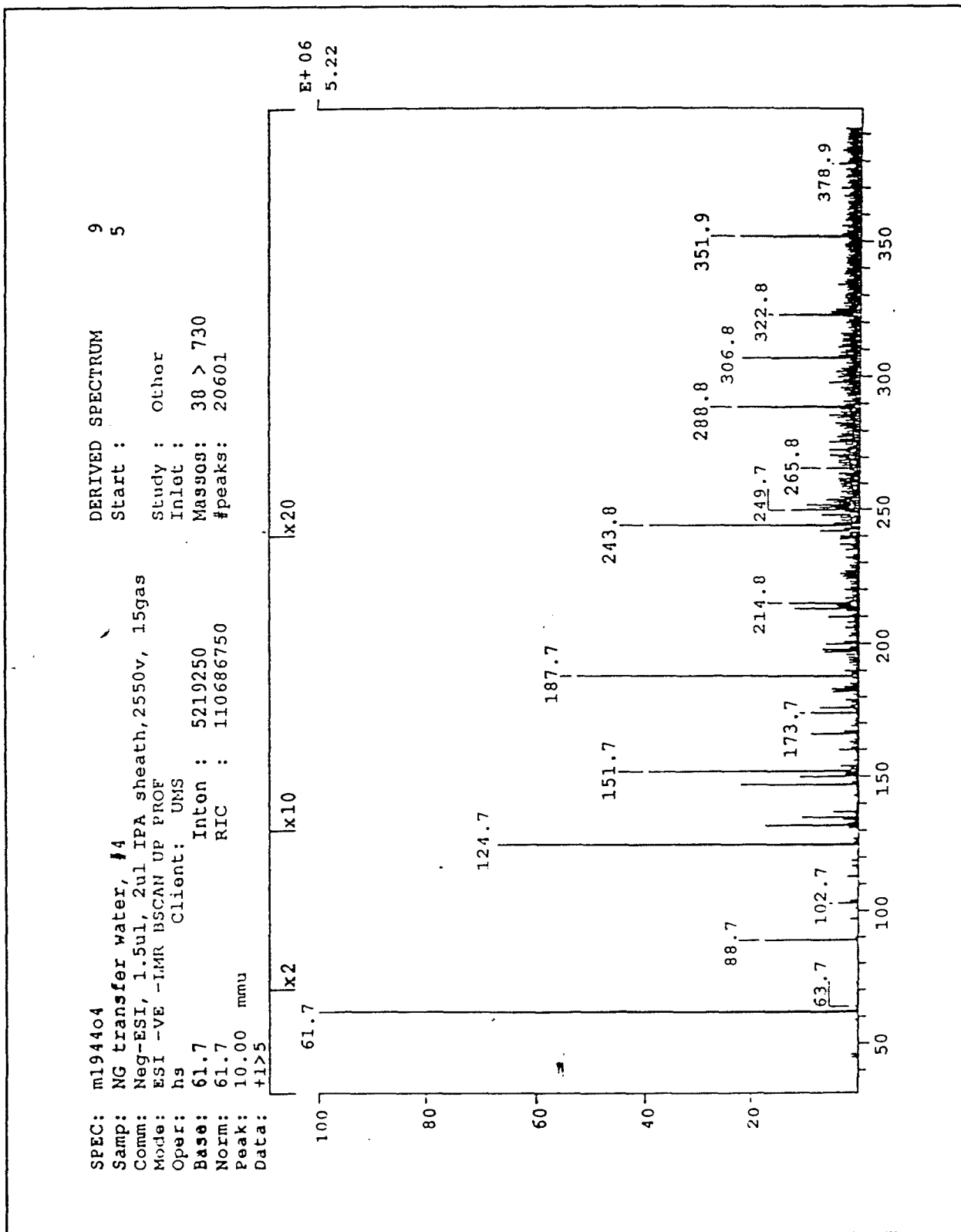
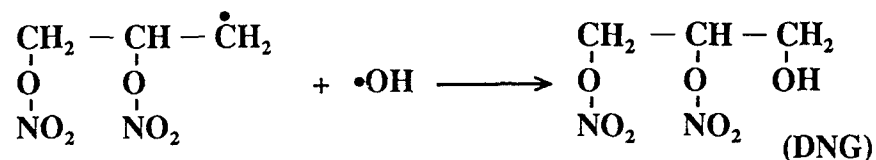


Figure 4: Electrospray-MS of partially treated (EB) sample

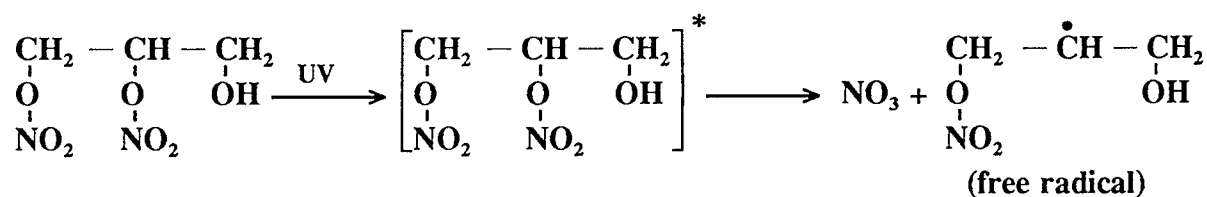
The free radicals produced in equation (2) can react with oxygen or water and undergo scission, or react with a hydroxyl radical that will add at the radical site. This reaction is confirmed by previous HPLC and our electrospray-MS work. Specifically, the electrospray-MS identified the dinitroglycerine, mononitroglycerine, and glycerol that are produced via the following path:

(7)

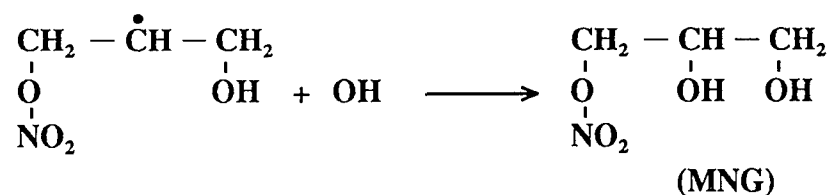


The dinitroglycerine undergoes further excitation, through the nitrate group, followed by ejection of the nitrate group and the production of a free radical (8,9). This process proceeds until all of the nitrate groups have been cleaved (10). As described previously, all of these species are observed in the electrospray-MS results.

(8)

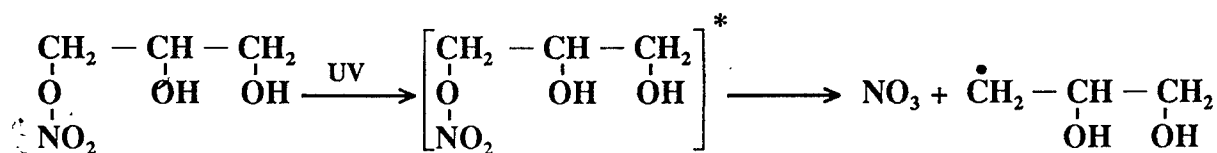


(9)



Likewise the mononitrate, excited through the nitrate chromophore, undergoes dissociation of the nitrate group like the dinitrate:

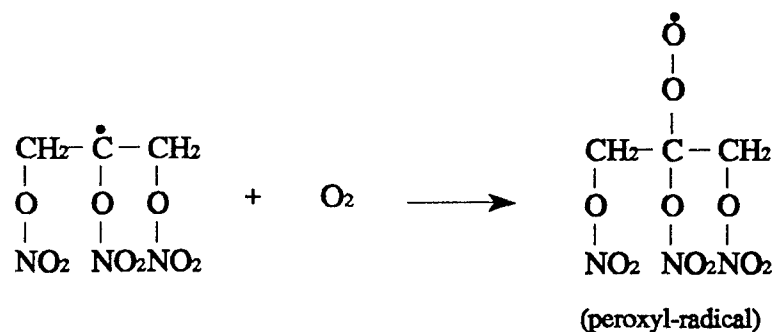
(10)



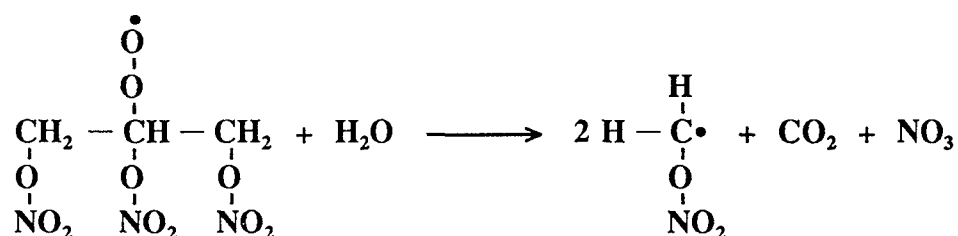
In addition to these reactions, the alkyl radicals can react with oxygen to form peroxy radicals

(11) that quickly fragment into methyl nitrate radicals, carbon dioxide, and nitrate (12).

(11)

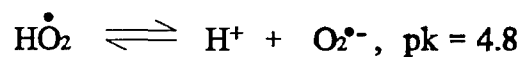


(12)



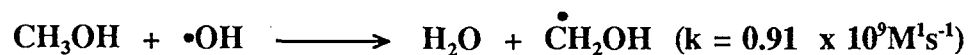
These reactions are, however, sensitive to many factors including pH. For example:

(13)



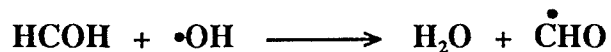
Although alcohols do not absorb light in the UV region and therefore will not undergo direct excitation by the UV treatment, they can undergo other reactions in the presence of chemically aggressive species. For example, methanol reacts with hydroxyl radicals to form water and the methanol radical:

(14)



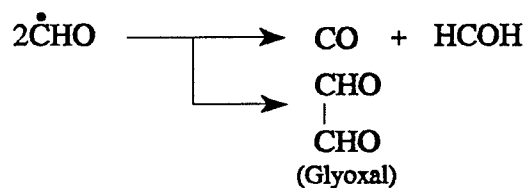
After a second reduction to formaldehyde by the hydroxyl radical, termination by disproportionation or dimerization can take place:

(15)



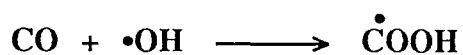
This byproduct can react with another free radical (for example itself) to create stable products like glyoxal or carbon monoxide:

(16)



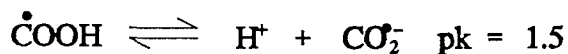
The carbon monoxide can react with the hydroxyl radical, to produce formic acid and oxalic acid --

(17)



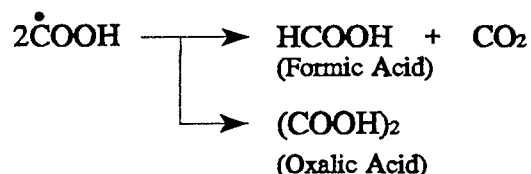
which is once again pH sensitive, and

(18)



can produce formic acid, oxalic acid, and carbon dioxide as products.

(19)

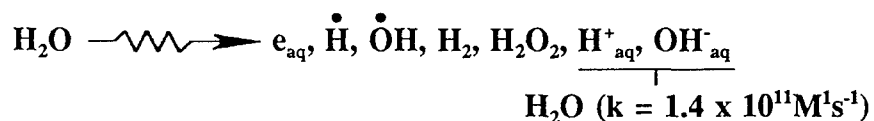


5.0 RADIOLYSIS IN THE PRESENCE OF O₂

5.1 Water Radiolysis

In the radiolysis of water, a number of species are formed in large quantities. They include the hydroxyl radical like the one produced by the degradation of hydrogen peroxide during the UV treatment process, plus other very aggressive reactants. Most notably these additional species include the solvated electron and the hydrogen radical.

(20)



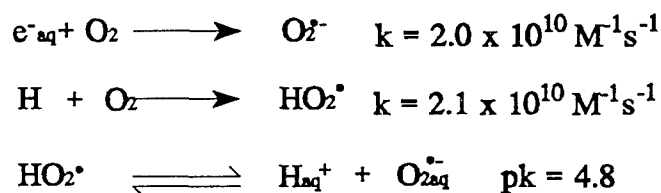
The production of these species is measured in terms of G-values (defined as the number of species produced per 100 eV absorbed). For the radiolysis of water, the total number of reactive species can be calculated by knowing the individual G-values (in the order as given above):

(21)

$$G = (2.7) + (0.6) + (2.8) + (0.45) + (0.75) \\ (\text{at pH} = 7)$$

In the presence of O_2 , both the solvated electron and the hydrogen radical are converted into peroxy radicals:

(22)



$$\text{At } pH \geq 7, \frac{(O_2^{\cdot-})}{(HO_2^{\cdot})} > 100$$

The reactive species in this case are: OH and $O_2^{\cdot-}$. With respect to the resultant attack of the hydroxyl radical, it can be described in exactly the same way as for the UV system resulting in the same radiolytic byproducts (and confirmed by GCMS as shown in Figure 5 through Figure 8).

6.0 QUALITATIVE AND QUANTITATIVE MEASUREMENT SUMMARY

6.1 Ammonia Measurements

Task 1.2 of this project (Ammonia Measurements) was originally proposed because ammonia is the ultimate byproduct for the destruction of nitrate esters, and therefore, represented a

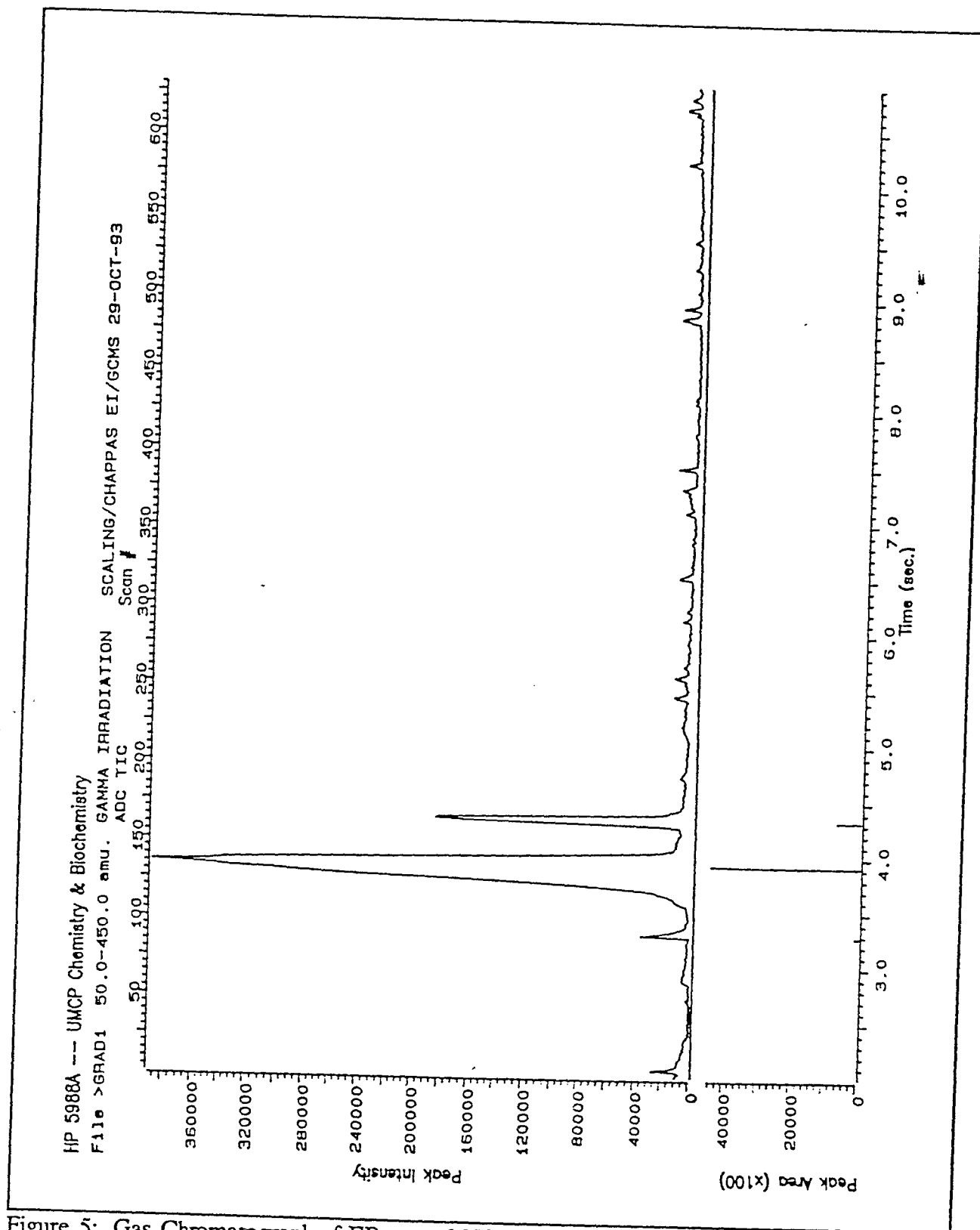


Figure 5: Gas Chromatograph of EB treated NG sample

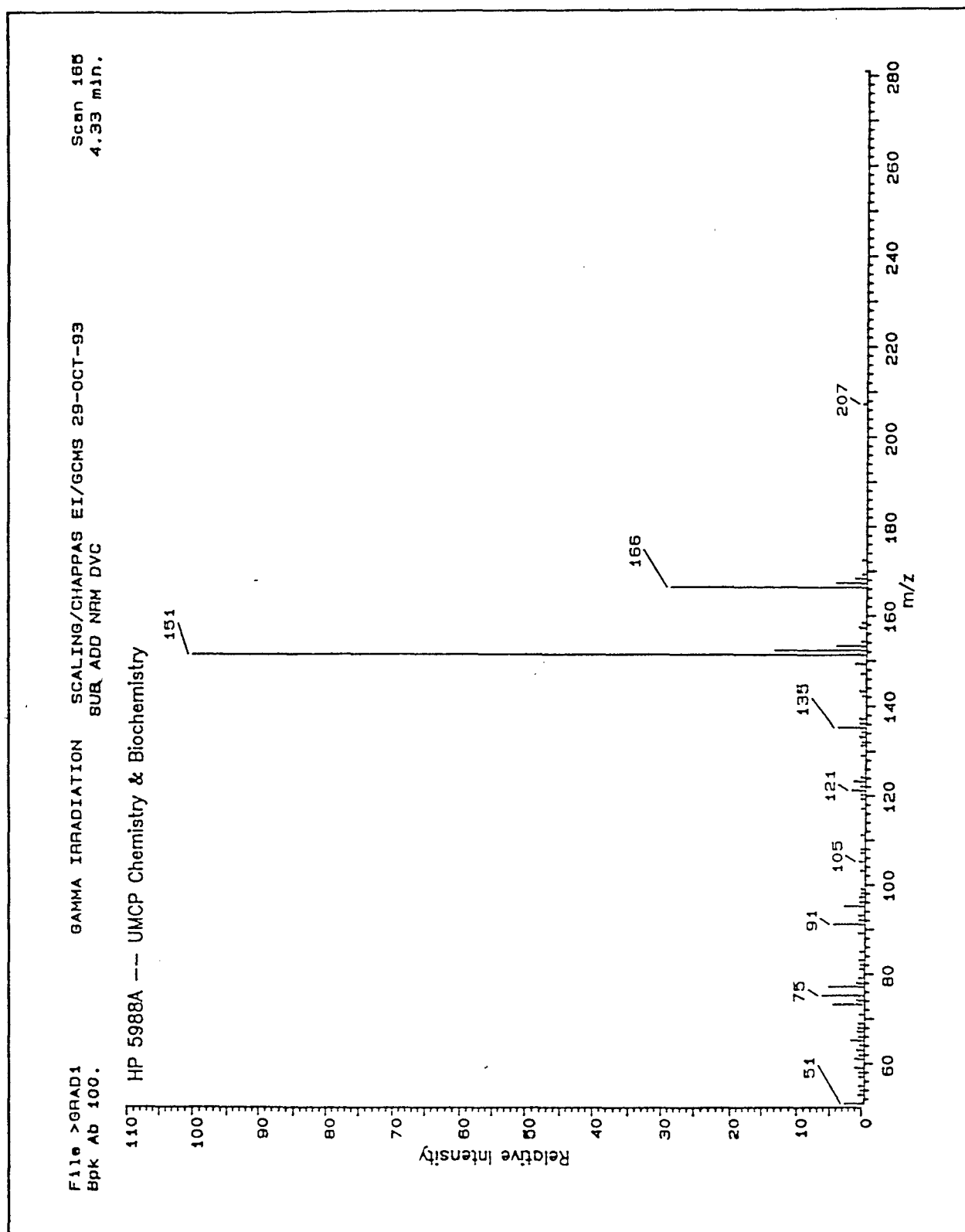


Figure 6: Mass Spectrum of EB treated NG sample, Scan 165

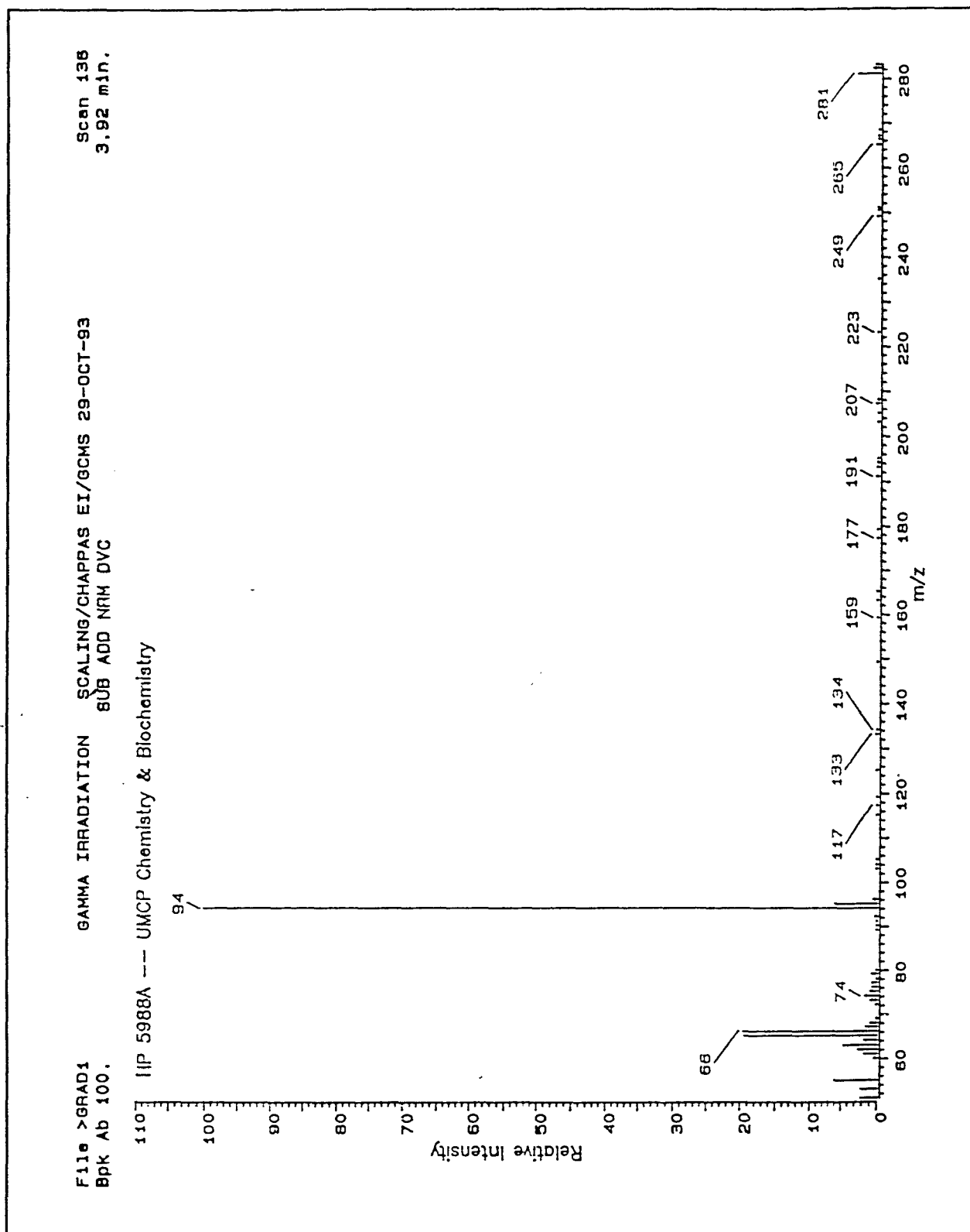


Figure 7: Mass Spectrum of EB treated NG sample, Scan 136

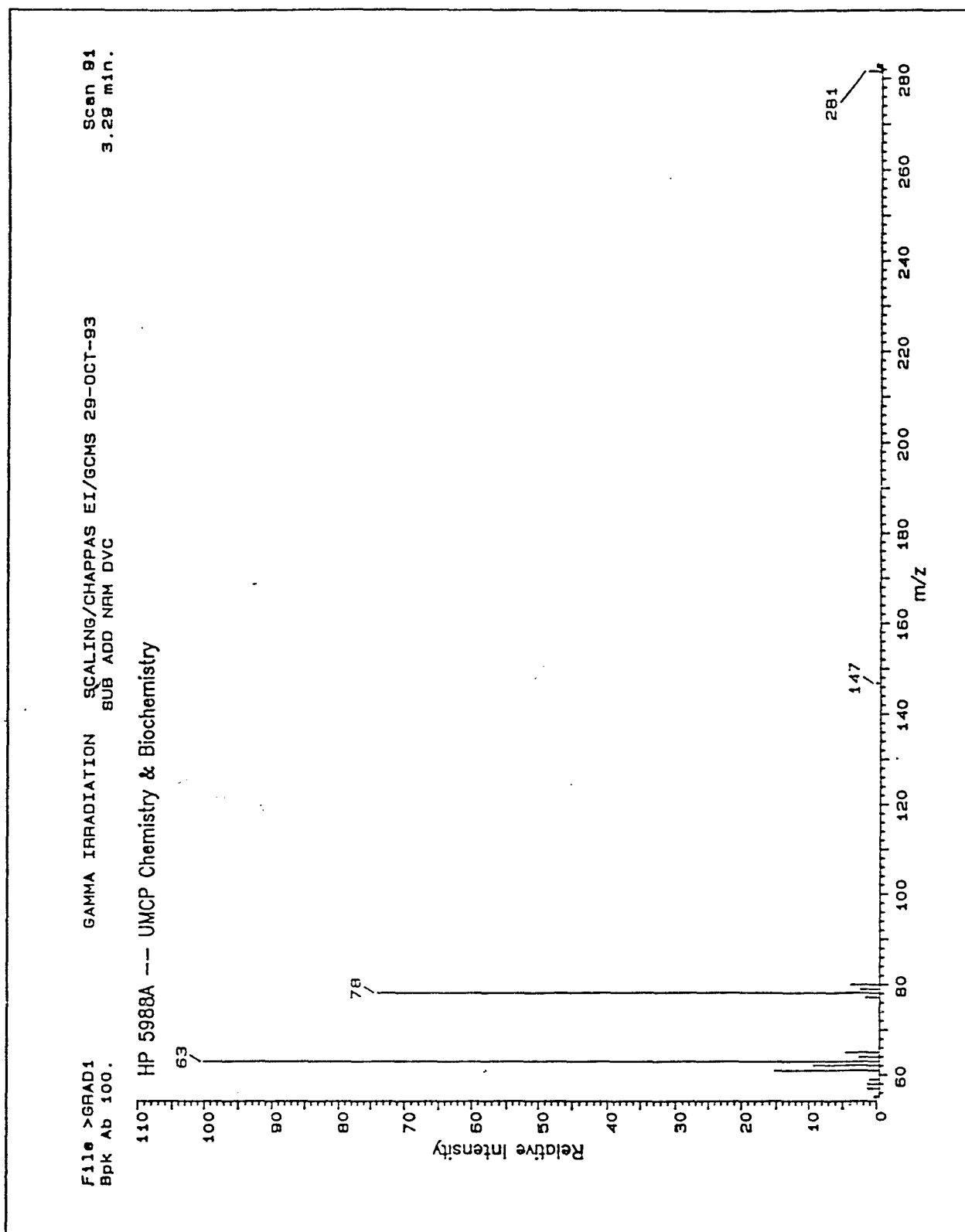


Figure 8: Mass Spectrum of EB treated NG sample, Scan 91

"decisive indicator for the effectiveness" of UV/EB techniques to reduce nitrates. It is clear from this research, however, that nitric acid is produced in large quantities and, in fact, is the predominant end product of the nitrate group. As a result, ammonia generation cannot be used as a "decisive" measure for the disappearance of nitroesters.

6.2 FTIR Measurements

An alternative technique was developed to directly measure the destruction of nitrate esters. By looking for all carbon-nitrate bond absorptions in the infrared region, the total nitrate ester concentration can be measured quickly and with less cost than by HPLC or GC-MS techniques. This technique does not differentiate between MNG, DNG, and NG. The FTIR evaluation has a significant advantage: FTIR can identify nitrate ester fragment, not just the specific nitroester for which HPLC might be calibrated. GC or GC-MS cannot be used at all, since the high temperature GC process degrades the nitrate ester.

6.3 MS Measurements

Electrospray and GC mass spectral techniques were applied to identify the degradation byproducts from UV and EB processed samples. Electrospray was used in an attempt to identify and quantify all of the NG fragments, the converted alcohols, acids, and any remaining nitrate esters in a single analysis. This is impossible with high temperature techniques such as GCMS that degrades the material during evaluation.

6.3.1 Electrospray

Electrospray evaluation of fully treated NG and PGDN samples show a series of inorganic clusters (identified in the appendix). Other than glycerine, no organic residues were detected. In untreated, and partially treated samples, glycerol, dinitroglycerine, and mononitroglycerine were detected in very small quantities. It was concluded that this technique could be used as a qualitative evaluation for the presence of some species but never for the quantitative measure of the waste water samples.

6.3.2 GC-MS

GCMS showed that the number and positions of GC peaks from untreated, UV treated, and EB treated samples were indistinguishable. For UV and EB samples, three species were identified that constitute >98.5% of the non-volatile byproducts.

7.0 FTIR PROCEDURE

7.1 Technical Approach

Organic nitrates used for explosives (i.e. nitric acid esters of alkane alcohols) have two properties that make FTIR spectroscopy a particularly effective method for their quantitative analysis:

1. they are much more soluble in CCl_4 than in water; and
2. as shown in Figure 1 and Figure 2, their IR spectra are characterized by three strong peaks associated with the nitrate group at 837, 1263, and 1650 cm^{-1} .

These facts have led to the development of the following procedure for the analysis of aqueous solutions of nitroglycerin and propylene glycol dinitrate in the 5-1000 ppm range. (Both higher and lower limits are possible depending on equipment.)

The IR spectrum is measured in the 800-2000 cm^{-1} region. Strong peaks are formed at 1265 and 1650 cm^{-1} . The exact positions are a function of pH and inert salt content but the variations are less than 10 cm^{-1} ; the ratio of the absorbance at two peaks (1265 and 1650 cm^{-1}) is constant at 2.30 ± 0.05 . Under these conditions the absorbance at both peaks for the first extraction contains more than 90% of all the organic nitrate (as shown from subsequent extractions).

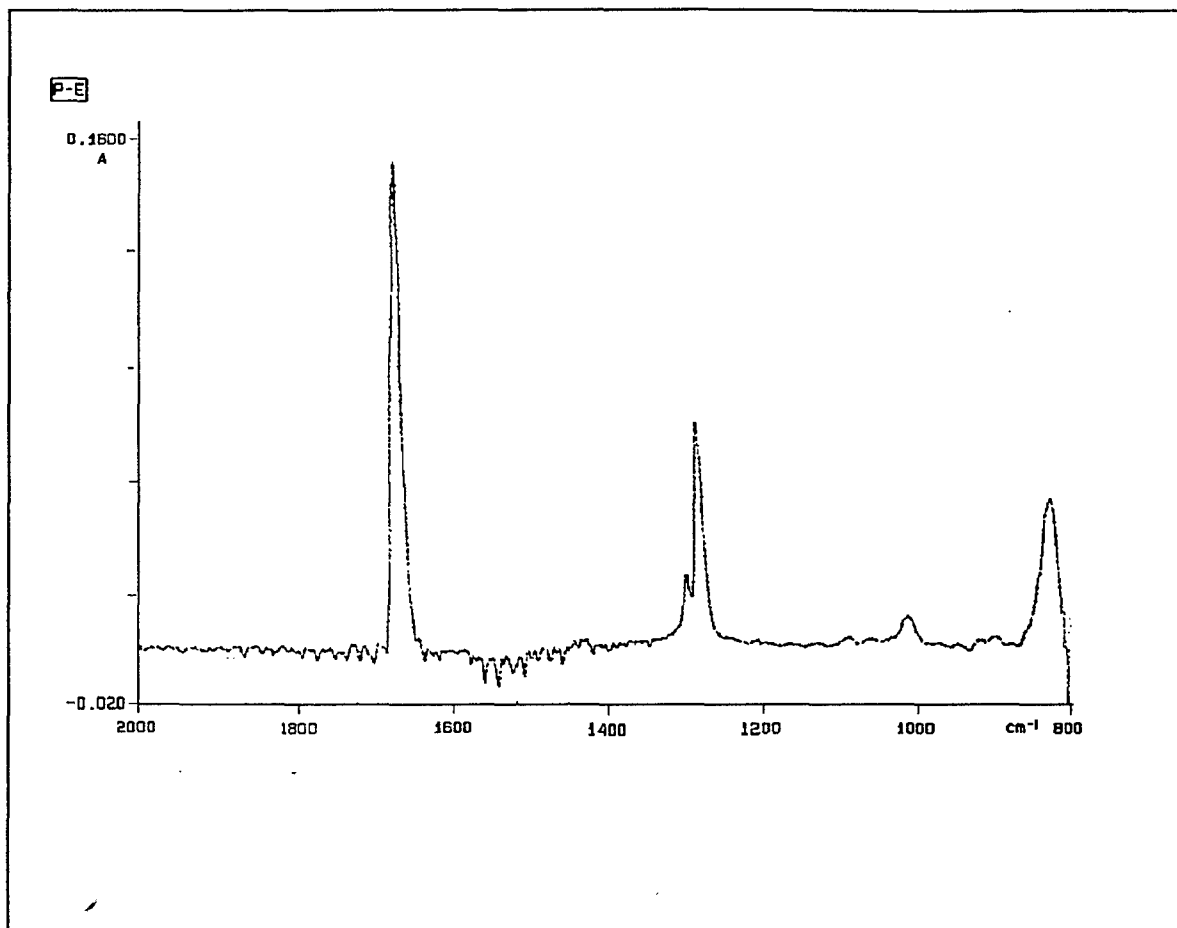


Figure 1: FTIR spectrum of NG in CCl_4 (0.1 mm optical path length).

7.2 Procedure

Typically 5.00 ml of CCl_4 are added to 5.00 ml of the aqueous solution of the organic nitrate in a separatory funnel (60 or 125 ml) with a PTFE stopper and stopcock. The funnel and contents are shaken vigorously for at least 20 seconds. A clear CCl_4 layer comes to rest in the bottom of the funnel. The aqueous layer contains some small suspended CCl_4 particles for up to 20 minutes; the settling of the suspended CCl_4 particles at the end of this period adds to the volume (slightly) but not the composition of the bottom layer. The stopper is then removed and the stopcock opened to drain 1-2 ml into a glass vial and capped. By means of a syringe, CCl_4 solution is withdrawn from the vial and discharged between the CsI plates (typically 3 mm thick) of a liquid sample holder for an FTIR Spectrophotometer (e.g. Perkin Elmer 1600 Series). The optical path in the liquid should be 0.1 mm for high concentration (50-1000 ppm) and up to 1 mm for low concentrations (5-50 ppm); the work reported here

Table IV: EXTINCTION COEFFICIENTS AT PEAKS

Organic nitrate	Peak ordinal number	Peak wave-number(cm^{-1})	$\epsilon(\text{L.mol}^{-1}.\text{cm}^{-1})^*$
NG	1	1665	1005
	2	1273	453
	3	831	302
PGDN	1	1651	1034
	2	1271	446
	3	837	274

* Because the first extraction contains at least 90% of the total organic nitrate, its ϵ is also at least 90% of its true value.

was obtained with the 0.1 mm spacing (Figure 3).

8.0 FTIR RESULTS

Upon development of the FTIR technique, Task 1.2 was modified to reflect the change of procedure. In accordance with the original task statement and the modified task statement, the technique has been used to measure the effectiveness of UV and EB treatments of nitroglycerine and propylene glycol dinitrate samples from standard and actual waste streams. The results are summarized in Table V. The UV streams were treated at Solarchem utilizing the UV system previously developed by Solarchem for NSWC Indian Head. The EB irradiated samples were treat-

Table V: RESIDUAL ORGANIC NITRATES IN TREATED ACTUAL WASTE STREAMS.

	UV* (ppm)	EB** (ppm)
NG Transfer	<MDL	7
NG Waste (Salts)	7	3
PGDN Transfer	10	136
PGDN Waste	62	93

* Full UV treatment

** Partial EB treatment

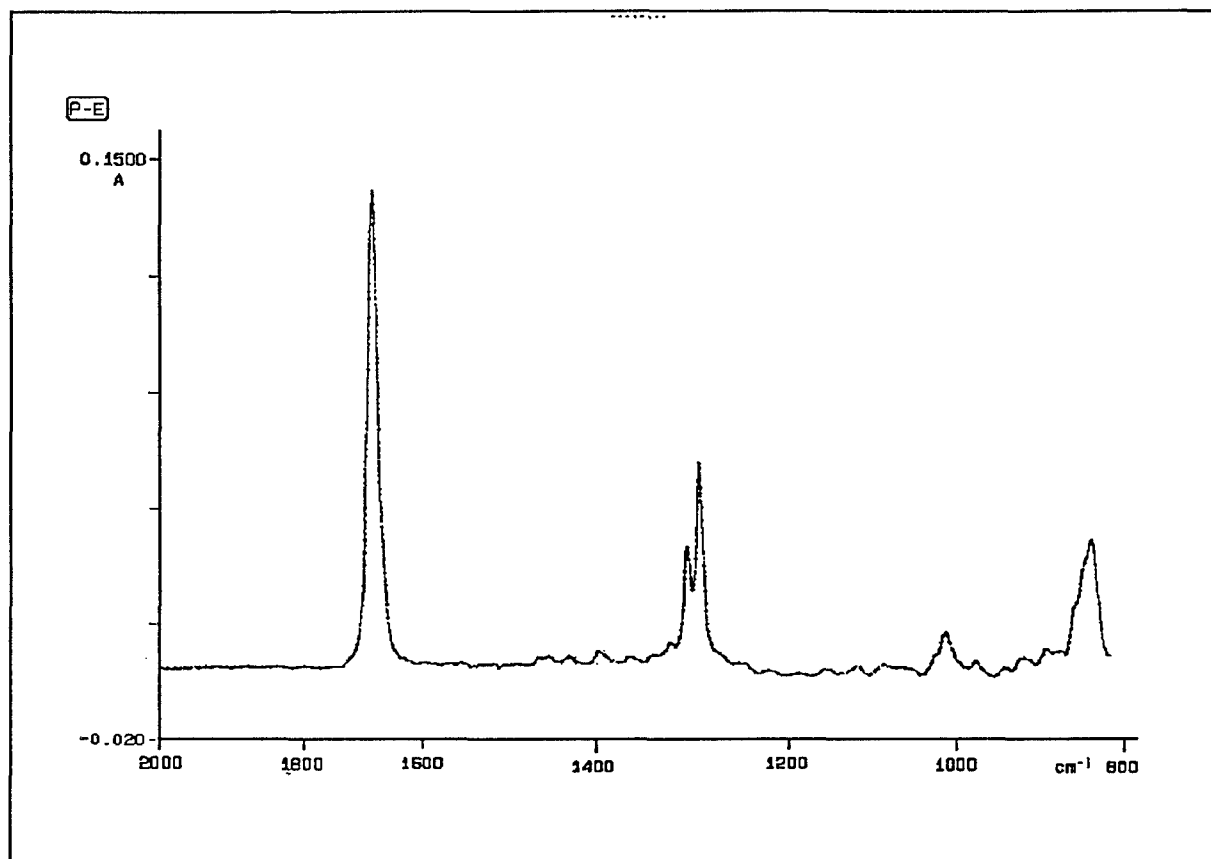


Figure 2: FTIR spectrum of PGDN in CCl_4 (0.1 mm optical path length).

ed to a dose below the dose required to destroy all of the nitrate esters so as to collect efficiency data regarding the process and to identify the intermediate and final byproducts (Task 1.1). In addition to the actual and standard waste streams, the technique was used to begin to evaluate the effect of dose, dose-rate, and pH on standard samples.

8.1 Effect of Dose and Dose-rate

Although the detailed evaluation of dose and dose-rate is scheduled for Phase II of the project (Task 2.1), preliminary evaluations of these parameters were collected (Task 1.2). The results (Figure 4) show that PGDN in water (pH of 9) can be reduced to trivial quantities with 50 kGy and to undetectable levels at 100 kGy. The same results were obtained for NG in water (Table II). The effect of dose-rate was evaluated by irradiating separate oxygen and nitrogen saturated samples. The results show that oxygen plays a small, but significant role in the destruction of the nitrate ester group. Not only does this information confirm that there is a

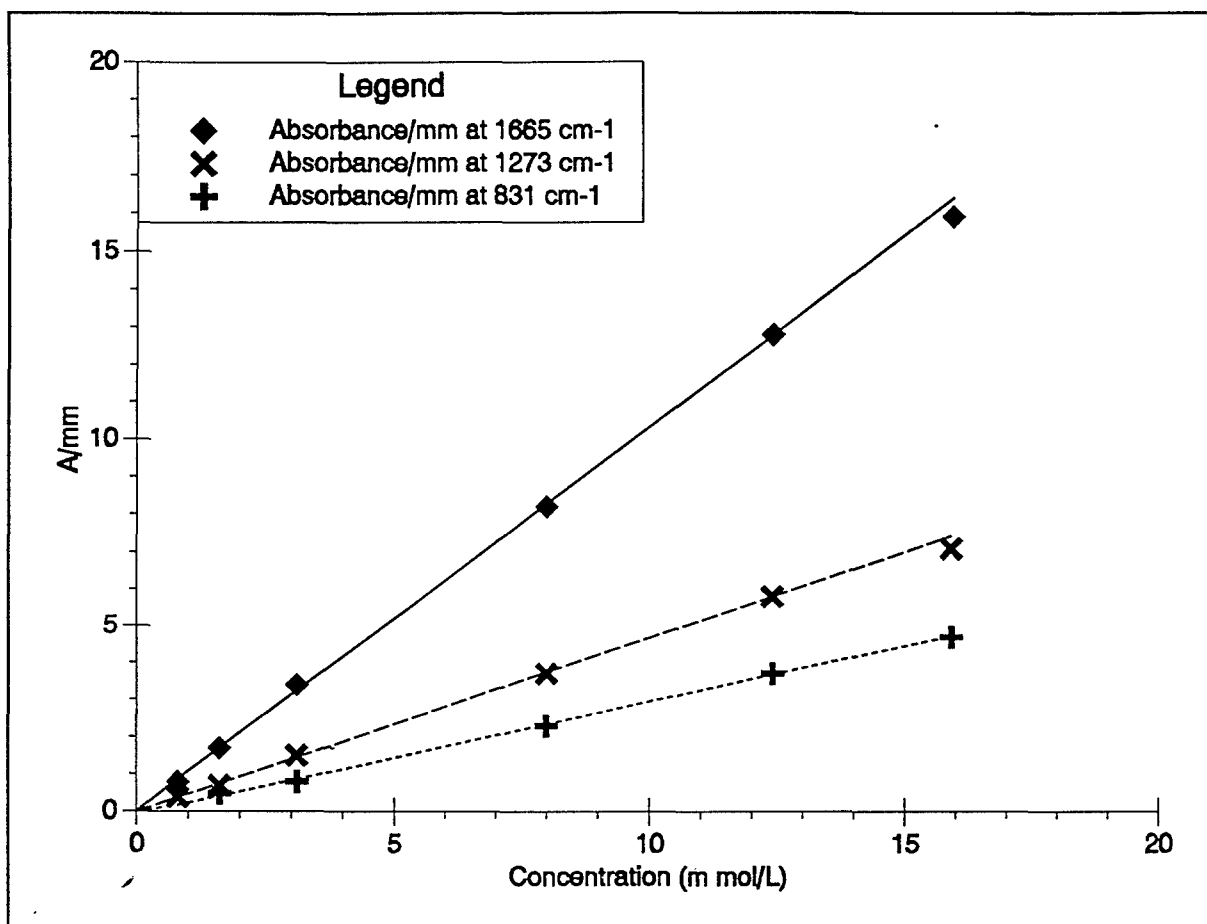


Figure 3: Organic nitrate concentration calibration for NG in water.

dose-rate effect, it also provides mechanistic insights into the chemistry. A detailed evaluation of dose and dose-rate will be compiled in Phase II.

8.2 Effect of pH

The radiation chemistry can be enhanced or sharply reduced by pH. The results for NG are summarized in Figure 5. The results for samples irradiated to a total absorbed dose of 25 kGy show that radiations effectiveness in destroying nitrate esters increases as pH is increased or if oxygen is removed from the system. The same trend was achieved at 50 kGy.

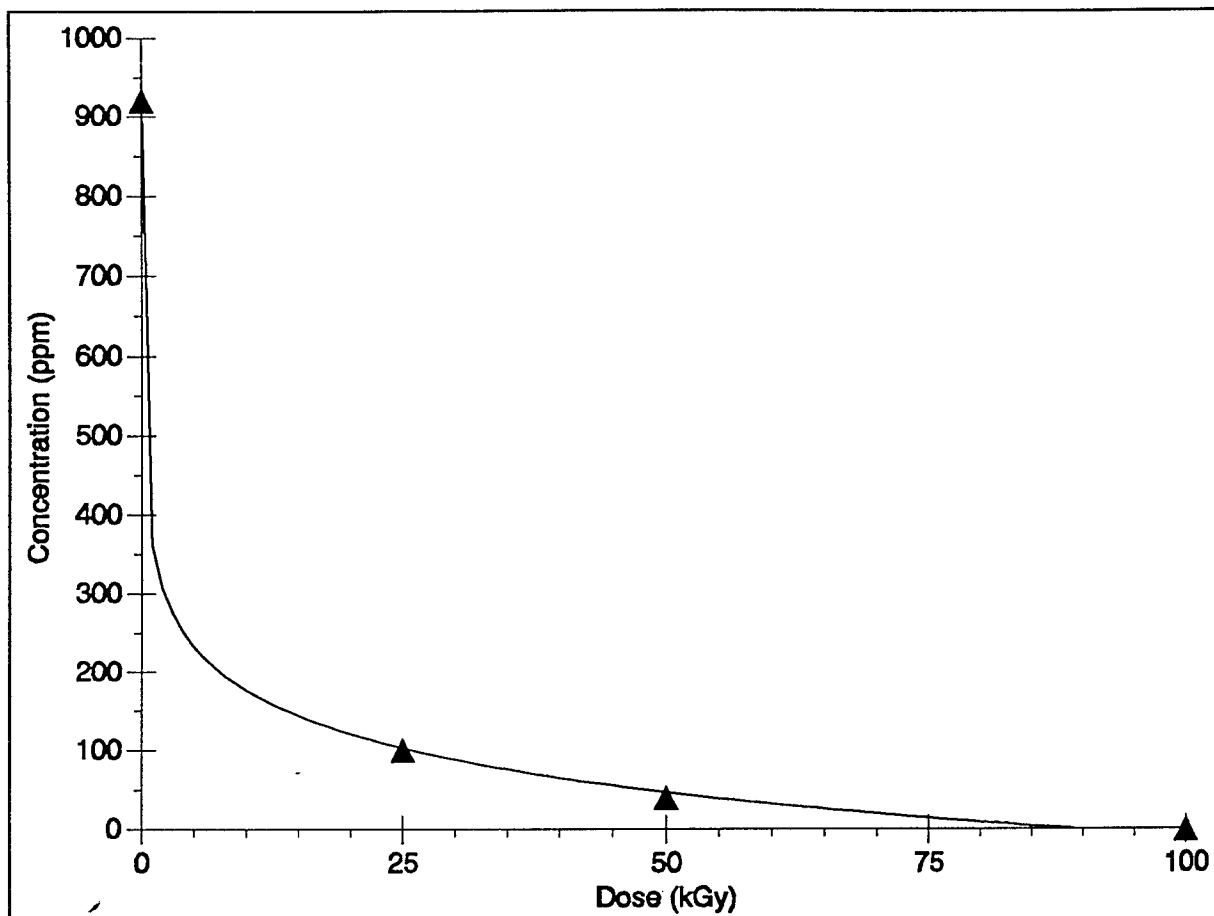
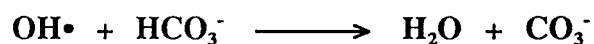


Figure 4: The effect of dose on waste PGDN.

8.3 Effect of Residual Salts

The reaction mechanisms cited above are based on pure aqueous solutions of the nitrate esters (plus added H_2O_2 or O_3). Real systems involve the presence of sodium salts of nitrate, sulfate, carbonate, and bicarbonate anions. Therefore it is important to understand the influence of these solutes with reactive species generated in the UV and electron irradiated samples.

For the UV systems, the initiating species are OH^\bullet and excited nitrate esters. The former reacts with HCO_3^- and $\text{CO}_3^{=}$ with a rate constant of $\sim 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.



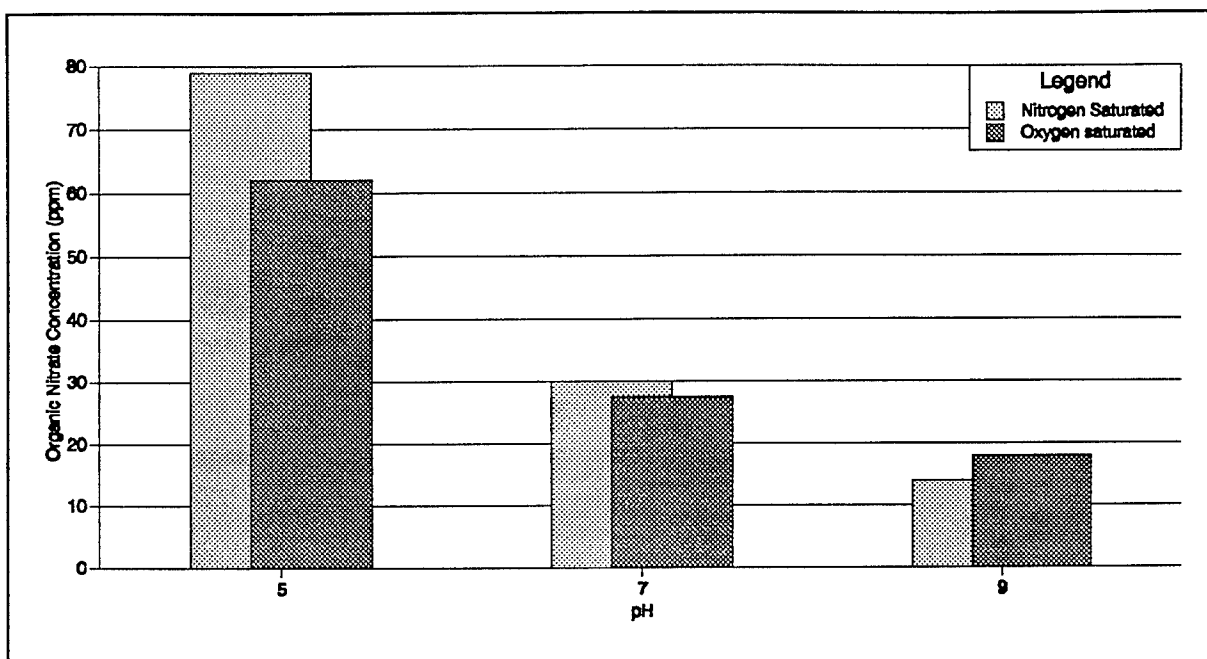
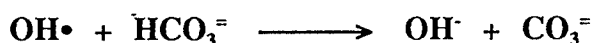


Figure 5: The effect of pH on the radiolytic destruction of NG.



Thus at high concentrations of the two anions (especially $\text{pH} > 9$), they are doubtless a complicating factor. At $\text{pH} \leq 7$, their influence is trivial. There is no reaction between OH and both the sulfate and nitrate ions, and the reactions of the excited ester with the OH is almost certainly unimportant. The aqueous nitrate ion does react with the organic free radicals but in a manner that is likely to enhance the destruction of some of them.

For the electron irradiated system, the two transient reducing species present are e_{aq} and H . Their reactions with sulfate, carbonate, and bicarbonate can be neglected, but the reactions of e_{aq} with NO_3^- is extremely rapid ($k \sim 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). At 3% inorganic nitrate, this is likely to be the predominant reaction in the system. The principal result is likely to be the nitrite ion which is easily oxidized by the OH . Here again, lower pH is beneficial in minimizing the complication. The H , which is favored relative to e_{aq} at low pH, has a much lower rate constant for the nitrate reduction. Of course lower aqueous nitrate is also helpful.

9.0 RADIATION SOURCES

9.1 Reliability

Industrial radiation sources are used in industry throughout the world. Chemical companies, rubber companies, and biomedical supply manufacturers use high powered EB machines in dirty, harsh, production environments. Without exception, EB machines have demonstrated their reliability, safety, and value. Modern EB machines use solid state circuitry and have no moving parts. A process for the treatment of water could be exceptionally reliable, since the equipment to move the water past an electron beam would consist of nothing more than a pump pushing water through pipes or over a weir.

9.2 Cost

Modern EB machines are available from a number of vendors in the U.S. and abroad. Low energy machines of the kind envisioned for application at Indian Head are simple transformers and, for the power and energy requirements of the Biazzi plant, might be available for as little as \$300,000. Shielding for such a device does require about two feet of concrete. However, there exist on station several buildings that are vacant and partially meet this requirement. Almost certainly, one processing facility would be sufficient to process all of the waste streams at Indian Head.

A 100 kW EB facility could process about 500 USG/hour of NG transfer water. With a 67% line to beam efficiency, the power cost would be about 0.3 kWh/USG or about half the price of UV techniques.

10.0 CONCLUSIONS

The UV/EB treatment of contaminated waste water is an extremely effective technique for the removal of nitrate esters. Earlier work demonstrated that UV treatment in the presence of peroxides could reduce the organic nitrate concentration below 1 ppm. This work confirms that

low dose EB treatment can achieve the same results with a lower energy cost and without the addition of hydrogen peroxide. Even in the presence of inorganic carbonates and bicarbonates, the nitrate contaminants can be effectively removed economically. In Phase II of the program, the advantages of oxygen, additives, and dose will certainly be effective in reducing the nitrate concentration for both wash and transfer waste streams to EPA acceptable levels at costs far below conventional or UV techniques.

This Phase I program also evaluated the kinds and yields of degradation byproducts that are produced in the UV and EB techniques. The mechanism was developed and confirmed by electrospray-MS, GCMS, and FTIR measurements. The results show that full treatment completely destroys the original nitrate ester, leaving behind nitric acid and glycerine. It is possible that small organic byproducts from the hydrolysis or oxidation process may be left behind but none were detected.

UV and EB treatment offer excellent opportunities for the low cost destruction of nitro ester contaminated waste water. In low volume applications, UV appears to have cost advantages over EB treatment. In large volume applications, however, or for the treatment of d with added salts, EB treatment appears to have significant cost advantages.

11.0 RECOMMENDATIONS

In this work, it is demonstrated that EB processing can destroy nitrate ester compounds in clean waste water (i.e. the nitrate ester and water alone) as well as waste water with buffers (i.e carbonates and bicarbonates) and just like UV processing, produces no measurable toxic byproducts.

Therefore, when fully developed in Phase II of this work, EB processing should offer a significant advantage over UV treatment, since:

1. The penetration of UV is limited by parasitic solutes that absorb in that wavelength region, and by suspended solids, some of which might be useful for adjustment of pH or for heterogeneous reactions at the solid-liquid interface. The same solutes and suspended solids are essential transparent to high energy

electrons. The latter deposit their energy in each component of the absorber in proportion to its weight fraction. Thus water, which is more than 90% of the waste stream absorbs 90% of the electron energy.

2. The chemical yield in terms of line power converted into chemical destruction is higher in electron processes. Preliminary evaluations indicate that about 0.3 kWh per USG of EB treatment is required while 0.5-1 kWh of UV is required.
3. UV and electron beams have been and still are in head-to-head competition. Whenever the process requires high mass throughput, the electron accelerator wins out. The reason it does not win in the case of low mass throughput is because of the relatively high capital cost of electron accelerator facilities. However the low energy consumption required for the desired chemical effects in this application, and the high volume of the throughput indicates that electron irradiation is a reasonable (and the probable) method of choice.

The nitrate ester content in effluent from ordnance manufacturing products is in the range of 0.3 - 6 g/liter with a mean concentration less than 0.01 molar. With a yield of oxidizing species of 0.4 micro-moles per joule, the minimum dose requirement is 25 kGy (25 J/kg or 2.5 Mrad) to produce sufficient species to completely oxidize the nitrate esters in the water. Gains achieved by additives can halve the dose requirements, but these would be balanced in part by process inefficiencies.

We are informed that the processing requirements for 1990 at the Indian Head Division alone add up to over seven million gallons or over fifty million pounds. Operating on a one shift basis, this is an application for a 100 kW machine. Even with an initial capital cost of \$800,000, this would probably cost less than any UV-based alternative.

The work of this Phase I program confirms the effectiveness of UV/EB decontamination processes to produce non-toxic byproducts. In Phase II, the chemistry of the process will be

advanced and the byproducts of the fully developed EB process will be evaluated. The techniques for evaluation of the EB process will also be used to evaluate the UV process in further detail.

At the end of Phase II, a fully developed process for the EB treatment will be described and the economics characterized. Based on our current understanding of the radiation chemistry of nitrate esters, EB treatment will offer significant advantages over all other techniques -- including UV. In addition, the process will almost certainly be an effective technique for the destruction of a broad range of other Indian Head and Defense Department waste streams.

11.1 Future Activities

In Phase II (year 2) of this project, the basic studies of the first phase will be extended to include an optimization of the EB process, especially with regard to dose and dose-rate. The tasks associated with this project are listed in the following paragraphs:

11.1.1 Sample preparation: Five (5) sample waste water streams will be prepared by NSWC-IHD for analysis in Phase 2. Ten gallons of each will be prepared and delivered to DAMILIC Corporation. The composition and pH of each will be provided by NSWC, Indian Head Division at the time of preparation.

11.1.1.1 Sample #1: Nitroglycerine in water (NG transfer water)

11.1.1.2 Sample #2: Nitroglycerine in water with salts (NG wash water)

11.1.1.3 Sample #3: Propylene glycol dinitrate in water (PGDN transfer water)

11.1.1.4 Sample #4: Propylene glycol dinitrate in water with salts (PGDN wash water)

11.1.1.5 **Sample #5:** Nitroglycerine, propylene glycol dinitrate, and salts in water
(NG/PGDN composite water)

11.1.2 **Sample Storage:** The samples will be stored in a refrigerator at a temperature recommended by NSWC-IH so as to minimize time dependent changes. The pH, conductivity, and organic nitrate concentration of each sample will be measured monthly.

11.1.3 **UV/EB Treatment:** The open processing system at SolarChem allowed the release of volatiles and thus precluded the establishment of a mass balance in the first phase of this project. In Phase 2, the samples will be sealed and processed. Although the closed system approach may change the chemistry of the system, it will permit a more complete mass balance to be established.

11.1.4 **UV Processing:** UV processing sealed vials will be accomplished at the NSWC-IHD UV Processing Facility. If this source is unavailable or unsuitable, an alternate UV source will be identified. Candidates include NIST, Fusion Systems, and the University of Vienna. Immediately before sample is prepared and sealed, the pH, conductivity, and organic nitrate concentration will be measured. In order to simulate the production process, hydrogen peroxide will be bubbled through the system prior to sealing.

11.1.5 **EB Processing:** The sealed vials will be irradiated at a contract irradiation facility of sufficient energy so as to fully penetrate the vial and deposit a uniform dose (max/min \leq 1.5). Candidate facilities include NIST, the University of Maryland, Irradiation Industries, and the National Polytechnical University (Quito, Ecuador). Immediately before the sample is prepared and sealed, the pH, conductivity, and organic nitrate concentration will be measured.

11.1.6 Gas Chromatography - Mass Spectroscopy Analyses: GC-MS will be used to establish a mass balance of the organic constituents in the UV/EB processed samples.

11.1.7 Waste Water Samples: Each of the 15 process streams (5 unirradiated, 5 EB irradiated, and 5 UV irradiated) will be evaluated by GC-MS for the volatile and non-volatile components of each sample. A quantitative and qualitative evaluation will be established. GC peaks that are both; (1) present in the untreated sample; and (2) have areas less than 1% of the total, will not be evaluated.

11.1.8 Standards: Where ever possible, reference materials will be acquired and quantitative baseline for the GC-MS evaluations will be established.

11.1.9 Inorganic Nitrate Measurements: A standard electrode capable of measuring inorganic nitrate concentrations will be calibrated and used to establish changes with time and treatment of the 10 process streams.

11.1.10 Organic Nitrate Measurements: FTIR will be used to establish the total organic nitrate concentration before and after treatment of the 10 process streams.

11.1.11 Mass Balance: Using the information gathered by GC-MS, pH, inorganic nitrate electrode, and FTIR a mass balance of the process by-products will be performed. The fates of organics and nitrates will be considered while the fates of water and oxygen will not.

11.1.12 Radiation Process Optimization: The irradiations will be performed in a manner so as to simulate an industrial process. They will be performed in air, at room temperature, and at equilibrium pH.

11.1.12.1 Dose Effect: The effect of dose on the concentration of total organic nitrates will be evaluated at 0, 50, 100, 150, and 200 kG.

11.1.12.2 **Dose Rate Effect:** The effect of dose on the concentration of total organic nitrates will be evaluated at three appropriate dose rates.

11.1.13 **Engineering Evaluation:** An engineering evaluation of a processing facility suitable for processing of the NSW-C-IHD waste streams will be performed. The report will include basic plan drawing of a treatment facility and estimates of construction and operating costs.

11.1.14 **Reports:** The following reports will be provided:

11.1.14.1 **Monthly:** A monthly report summarizing the work of the previous month will be prepared and submitted by the 15th of the following month.

11.1.14.2 **Final:** A final report summarizing the work will be prepared and submitted within 30 days after the end of the project.

1.0 REFERENCES:

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APPENDIX

FTIR DATA FOR LINAC-IRRADIATED 50%-SATURATED NG
WITH DIFFERENT pH, ENVIRONMENTS & ABSORBED DOSE

OPEN TO ATMOSPHERE, UNIRRADIATED					
Sample ID		pH before irradiation	Storage days before irradiation	A/mm	
				1664cm ⁻¹	1273cm ⁻¹
N10A5U0	1	5.3	0	1.063	0.473
	2	5.3	0	1.084	0.483
	M			1.074	0.478
	SD			0.011	0.005
N10A7U0	1	7.2	0	1.014	0.464
	2	7.2	0	1.008	0.451
	M			1.011	0.458
	SD			0.003	0.002
N10A7U0	1		48	0.988	0.443
	2		48	1.007	0.448
	M			0.999	0.446
	SD			0.011	0.003
N10A9U0	1	9.02	0	1.014	0.451
	2	9.02	0	1.035	0.448
	M			1.025	0.450
	SD			0.011	0.002
N10A9U0	1	9.00	1	0.999	0.432
	2	9.00	1	0.988	0.438
	M			0.994	0.435
	SD			0.006	0.003

NITROGEN SATURATED NG @ 25 kGy ELECTRON BEAM					
Sample ID		ppH before irradiation	Storage days before irradiation	A/mm	
				1664cm ⁻¹	1273cm ⁻¹
N10N5E1	1	5.3	48	0.101	0.047
	2	5.3	48	0.098	0.046
	M			0.100	0.047
	SD			0.002	0.0005
N10N7E1	1	7.2	48	0.071	0.033
	2	7.2	48	0.059	0.033
	M			0.065	0.033
	SD			0.006	0.000
N10N9E1	1	9.02	0	0.034	0.017
	2	9.02	0	0.030	0.017
	M			0.032	0.017
	SD			0.002	0.000

OXYGEN SATURATED NG @ 25kGy ELECTRON BEAM					
Sample ID		pH before irradiation	Storage days before irradiation	A/mm	
				1664cm ⁻¹	1273cm ⁻¹
N1005E1	1	5.3	48	0.058	0.036
	2	5.3	48	0.065	0.033
	M			0.062	0.035
	SD			0.004	0.0015
N1007E1	1	7.2	48	0.061	0.031
	2	7.2	48	0.065	0.032
	M			0.063	0.032
	SD			0.002	0.0005
N1009E1	1	9.02	0	0.031	0.021
	2	9.02	0	0.028	0.021
	M			0.030	0.021
	SD			0.0015	0.000

NITROGEN SATURATED NG @ 50kGy ELECTRON BEAM					
Sample ID		pH before irradiation.	Storage days before irradiation.	A/mm	
				1664 cm ⁻¹	1273 cm ⁻¹
N10N5E2	1	5.3	48	N/A	0.005
	2	5.3	48	N/A	0.008
	M				0.007
	SD				0.0015
N10N7E2	1	7.2	48	N/A	0.011
	2	7.2	48	N/A	0.012
	M				0.012
	SD				0.0005
N10N9E2	1	9.02	0	N/A	no peak
	2	9.02	0	N/A	no peak
	M				
	SD				

Radiation Induced Decomposition of Wastewaters Containing Nitroglycerine

- A. NG - transfer water (containing carbonates)
- B. NG - wash water (carbonates removed by H_2SO_4)
- C. PGDN - transfer water (containing carbonates)
- D. PGDN - wash water (carbonates removed)

Remark: The above water samples were irradiated with a dose of 100 kGy (10 MRad) and the products were analyzed by : "Negative ion electrospray mass spectrometry" method.

<u>ad. A : NG (with carbonates)</u>	
<u>Mass-Nr.</u>	<u>Compound</u>
46	NO_2^-
61.7	NO_3^-
88.7	$CH_2OH \cdot CHO \cdot CH_2O^-$
124.7	$NO_3^- \cdot HNO_3$
151.7	$CH_2OH \cdot CHO \cdot CH_2O^- + HNO_3$
187.7	$NO_3^- \cdot (HNO_3)_2$
214.8	$CH_2OH \cdot CHO \cdot CH_2O^- + (HNO_3)_2$
288.7	$NG \cdot HNO_3$

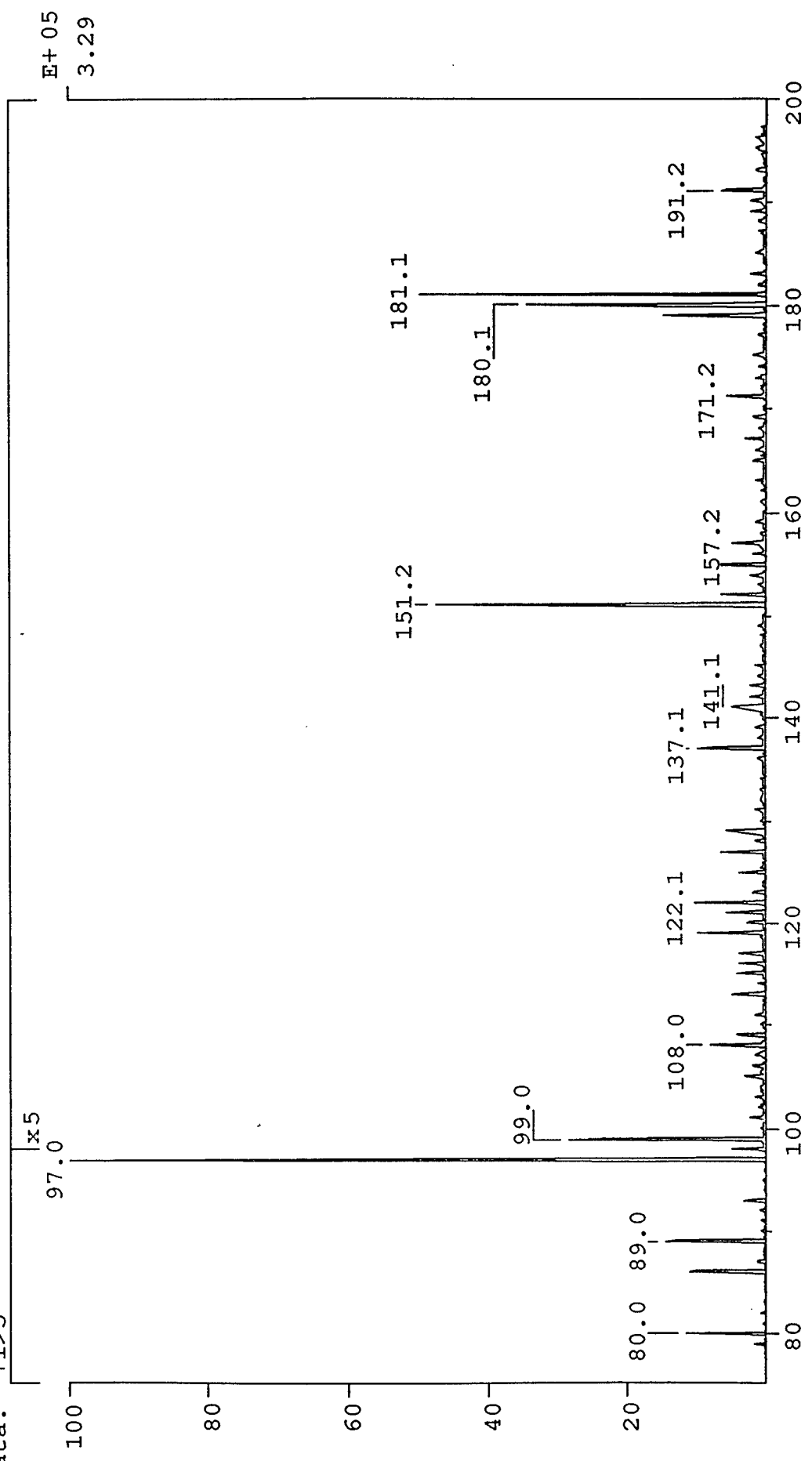
ad B : NG wash water - Carbonates removed by H_2SO_4 (precipitation to Ca)	
<u>Mass-Nr.</u>	<u>Compound</u>
46	NO_2^-
61.7	NO_3^-
119	NaSO_4^-
146	$\text{NaNO}_3\text{NO}_3^-$
260.7	$\text{NaSO}_4^-\text{Na}_2\text{SO}_4$
403.6	$\text{NaSO}_4^-(\text{Na}_2\text{SO}_4)_2$
544.7	$\text{NaSO}_4^-(\text{Na}_2\text{SO}_4)_3$

ad C : PGDN transfer water (with carbonates)	
<u>Mass-Nr.</u>	<u>Compound</u>
46	NO_2^-
61.7	NO_3^-
146.7	$\text{NaNO}_3\text{NO}_3^-$
231.7	$\text{Na}(\text{NO}_3)_2\text{NO}_3^-$
288.7	$\text{CH}_2\text{OHO}_2\text{CHONO}_2 \cdot \text{CH}_2\text{O} \cdot \text{HNO}_3$

ad D : PGDN wash water (carbonates removed)	
<u>Mass-Nr.</u>	<u>Compound</u>
46	NO_2^-
61.7	NO_3^-
96.7	HSO_4
146.7	$\text{NaNO}_3 \cdot \text{NO}_3^-$
231.7	$\text{Na}(\text{NO}_3)_2 \cdot \text{NO}_3^-$
288.6	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_2$
317	$\text{NO}_3^- (\text{NaNO}_3)_3$
373.6	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_3$
401.6	$\text{NO}_3^- (\text{NaNO}_3)_4$
458.7	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_4$
486.7	$\text{NO}_3^- (\text{NaNO}_3)_5$
543.6	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_5$
572	$\text{NO}_3^- (\text{NaNO}_3)_6$
630	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_6$
656.7	$\text{NO}_3^- (\text{NaNO}_3)_7$
713.9	$\text{NaSO}_4 \cdot (\text{NaNO}_3)_7$

SPEC: mas79305
Samp: standard, C 1,2,3 7-15-93
Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
Mode: ESI -VE -LMR BSCAN UP PROF
Oper: jl/hs Client: mass
Base: 62.0 Inten: 2529000
Norm: 97.0 RIC: 52143250
Peak: 10.00 mmu
Data: +1>5

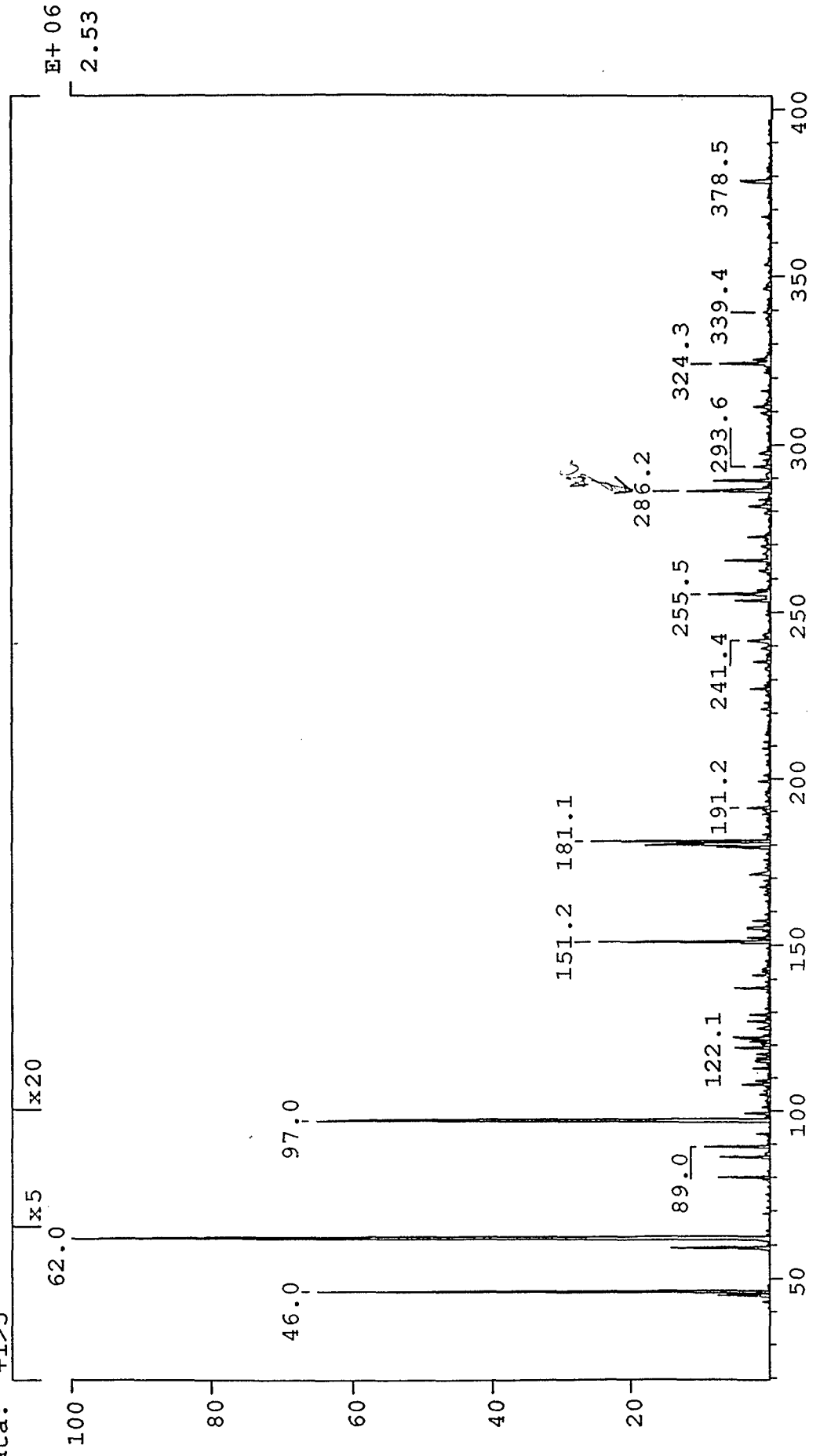
DERIVED SPECTRUM 9
Start: 5
Study: water samples
Inlet:
Masses: 38 > 626
#peaks: 7621



E+ 05
3.29

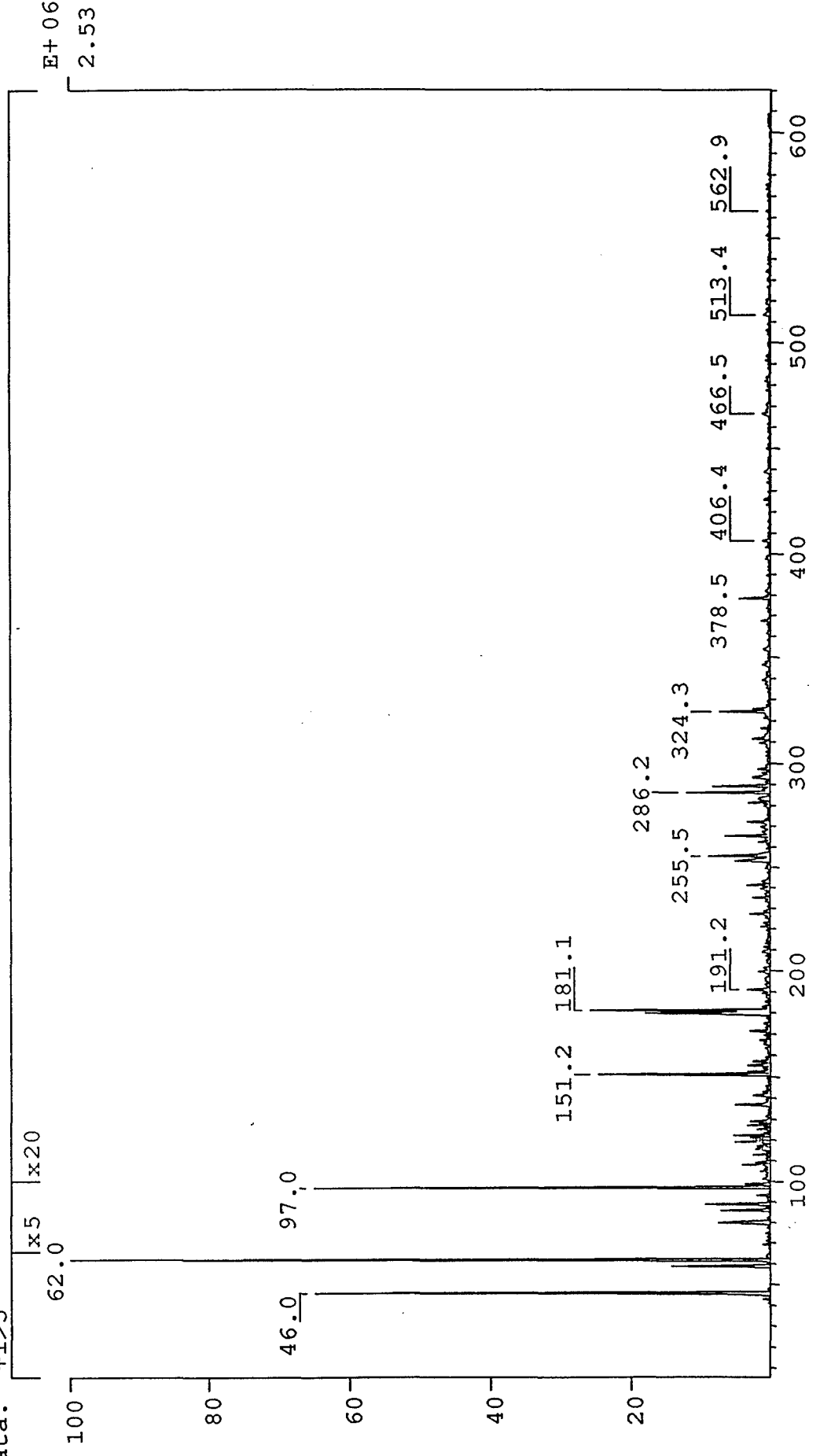
SPEC: mas793o5
 Samp: standard, C 1,2,3 7-15-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: jl/hs Client: mass
 Base: 62.0 Inten : 2529000
 Norm: 62.0 RIC : 52143250
 Peak: 10.00 mmu
 Data: +1>5

DERIVED SPECTRUM 9
 Start : 5
 Study : water samples
 Inlet :
 Masses: 38 > 626
 #peaks: 7621



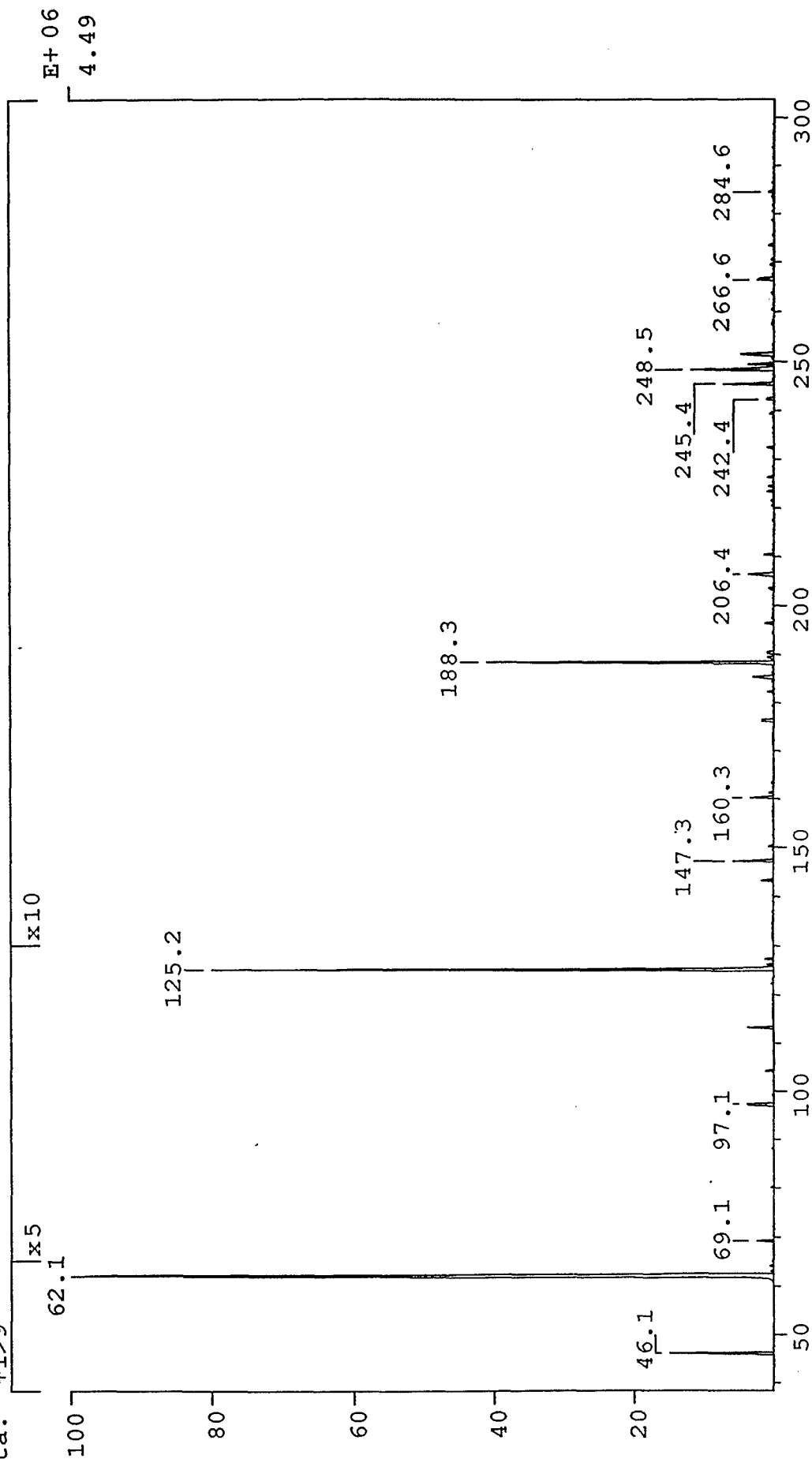
SPEC: mas793o5
 Samp: standard, C 1,2,3 7-15-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: jl/hs Client: mass
 Base: 62.0 Inten : 2529000
 Norm: 62.0 RIC : 52143250
 Peak: 10.00 mmu
 Data: +1>5

DERIVED SPECTRUM 9
 Start : 5
 Study : water samples
 Inlet :
 Masses: 38 > 626
 #peaks: 7621



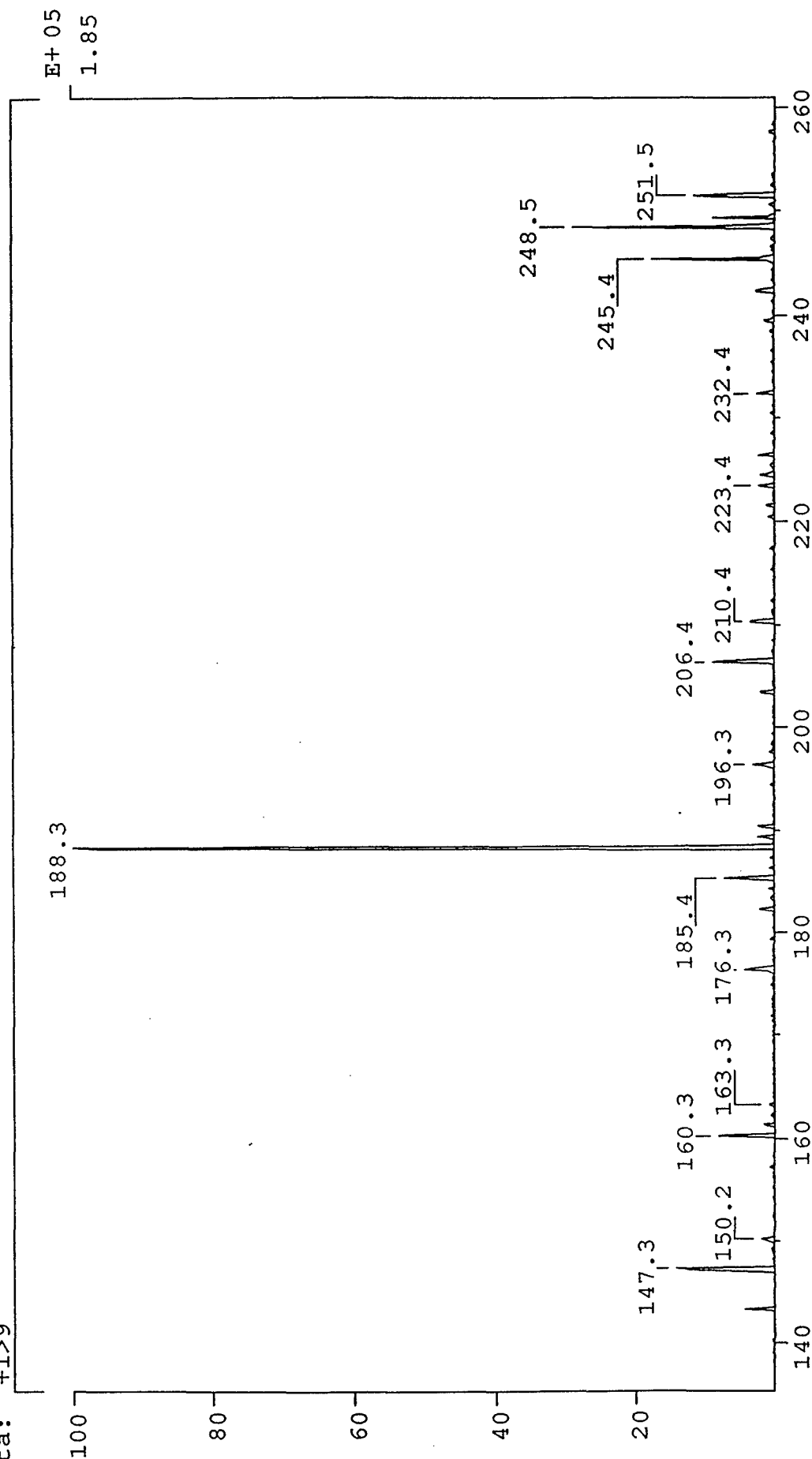
SPEC: mas79303
 Samp: 343-2-F NG treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: jl/hs Client: mass
 Base: 62.1 Inten: 4489000
 Norm: 62.1 RIC: 74300750
 Peak: 10.00 mmu
 Data: +1>9

28-Jul-93
 DERIVED SPECTRUM
 Start: 15:54:40
 Study: water samples
 Inlet:
 Masses: 38 > 633
 #peaks: 8381



SPEC: mas79303
 Samp: 343-2-F NG treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: jl/hs Client: mass
 Base: 62.1 Inten: 4489000
 Norm: 188.3 RIC: 74300750
 Peak: 10.00 mmu
 Data: +1>9

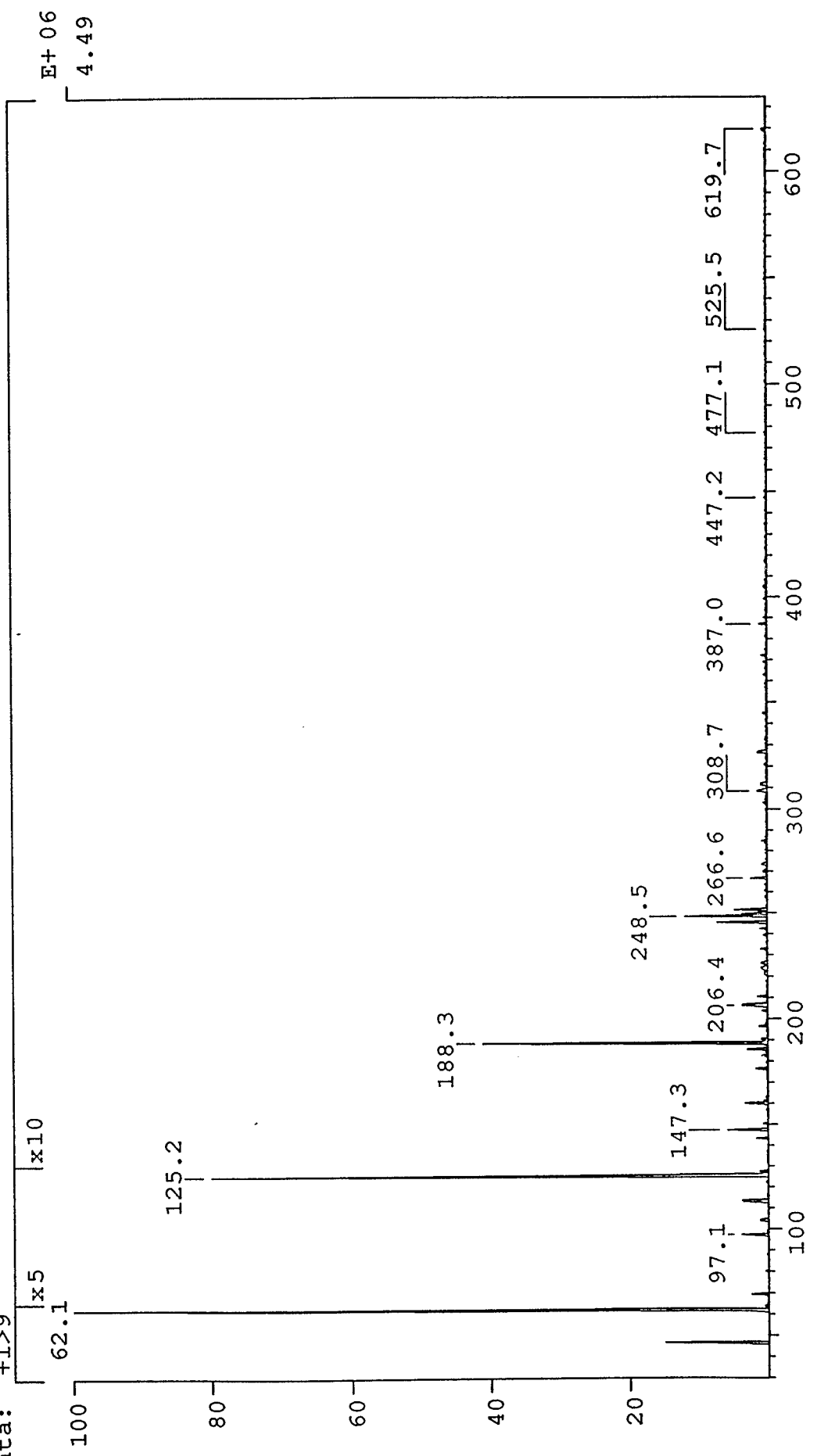
28-Jul-93
 DERIVED SPECTRUM 9
 Start: 15:54:40 12
 Study: water samples
 Inlet:
 Masses: 38 > 633
 #peaks: 8381



SPEC: mas793o3
 Samp: 343-2-F NG treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: j1/hs Client: mass
 Base: 62.1 Inten: 4489000
 Norm: 62.1 RIC: 74300750
 Peak: 10.00 mmu
 Data: +1>9

28-Jul-93

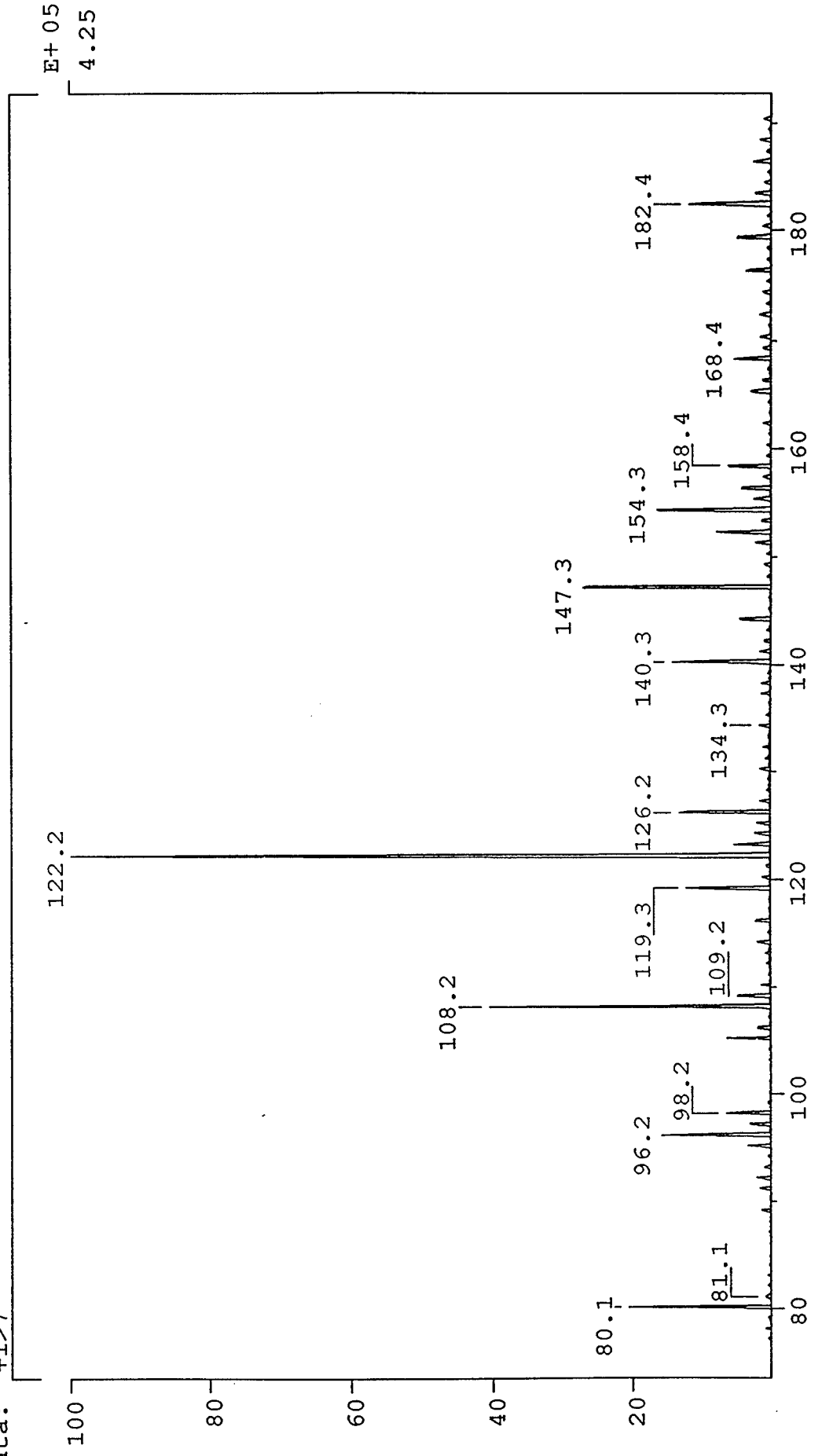
DERIVED SPECTRUM 9
 Start: 15:54:40 12
 Study: water samples
 Inlet:
 Masses: 38 > 633
 #peaks: 8381



SPEC: mas79302
Samp: 343-3-F PGDN treated 7-12-93
Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
Mode: ESI -VE -LMR BSCAN UP PROF
Oper: jl/hs Client: mass
Base: 62.1 Inten: 3119500
Norm: 122.2 RIC: 65561750
Peak: 10.00 mmu
Data: +1>7

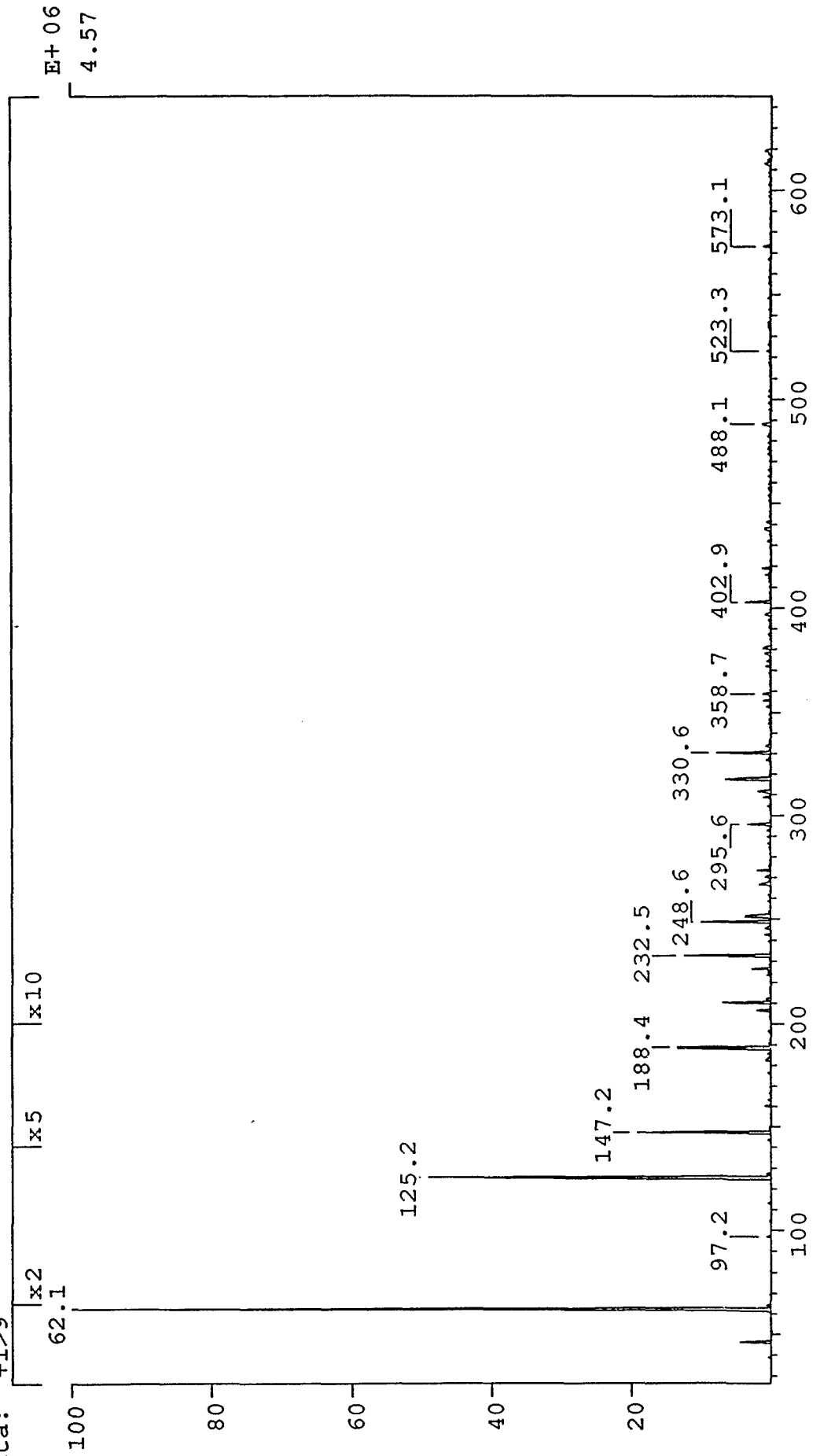
28-Jul-93
DERIVED SPECTRUM
Start: 15:40:27
Study: water samples
Inlet:
Masses: 38 > 633
#peaks: 12784

9
12



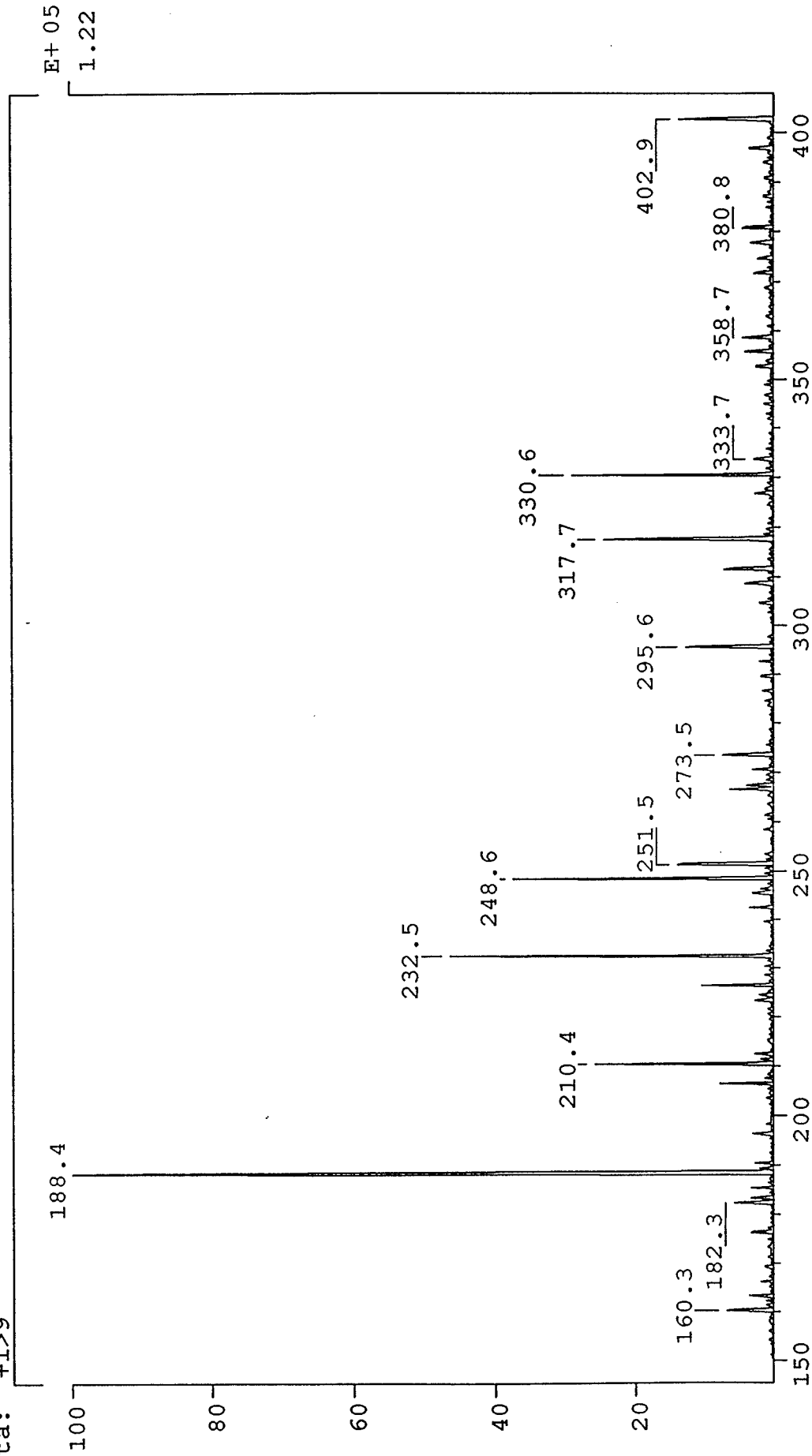
SPEC: mas79301
 Samp: 343-4-F PGDN treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: j1 Client: mass
 Base: 62.1 Inten : 4574000
 Norm: 62.1 RIC : 85654500
 Peak: 10.00 mmu
 Data: +1>9

28-Jul-93
 DERIVED SPECTRUM
 Start : 14:50:23
 Study : water samples
 Inlet :
 Masses: 38 > 633
 #peaks: 10225



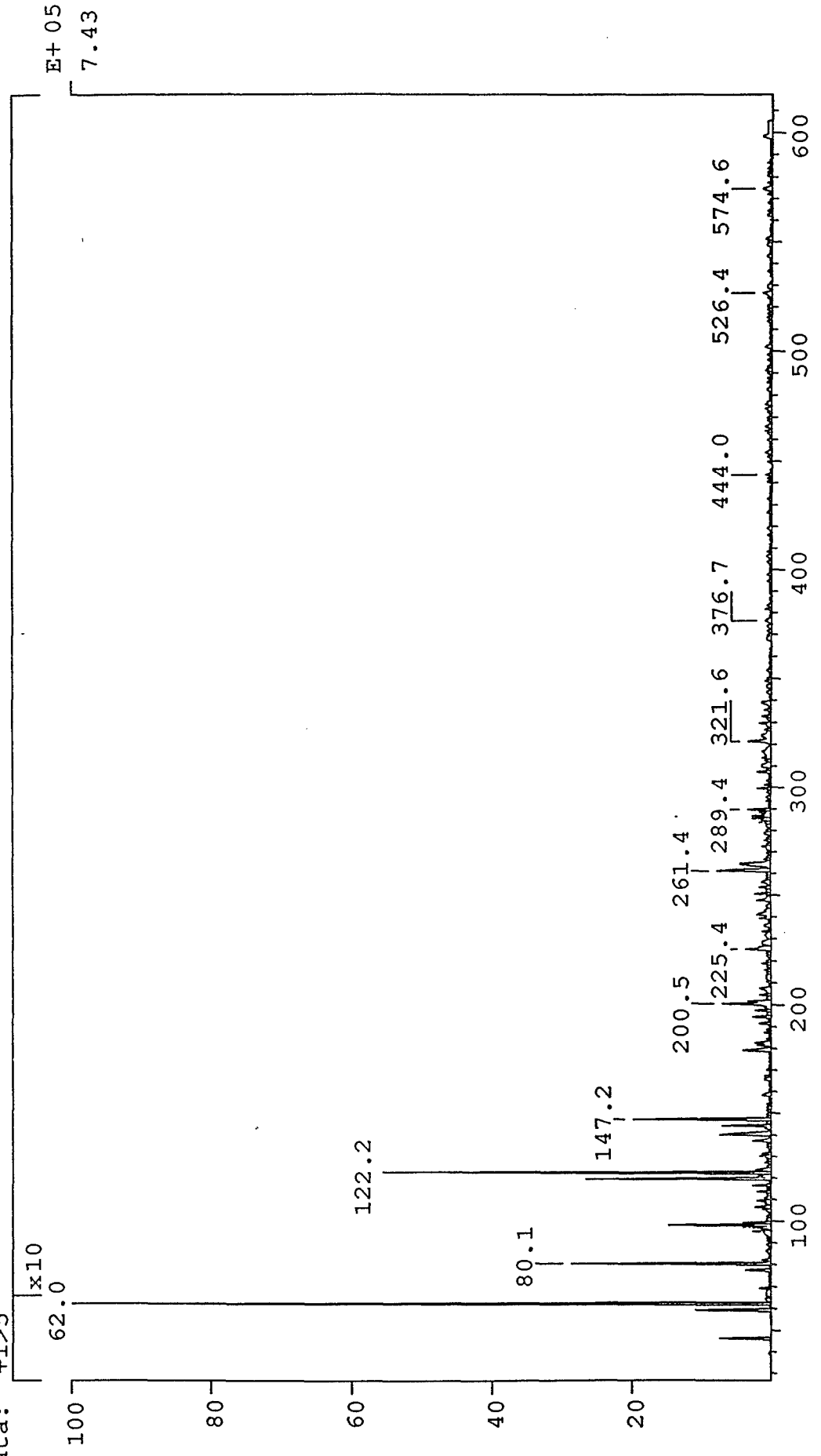
SPEC: mas79301
 Samp: 343-4-F PGDN treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: j1 Client: mass
 Base: 62.1 Inten: 4574000
 Norm: 188.4 RIC: 85654500
 Peak: 10.00 mmu
 Data: +1>9

28-Jul-93
 DERIVED SPECTRUM
 Start: 14:50:23
 Study: water samples
 Inlet:
 Masses: 38 > 633
 #peaks: 10225



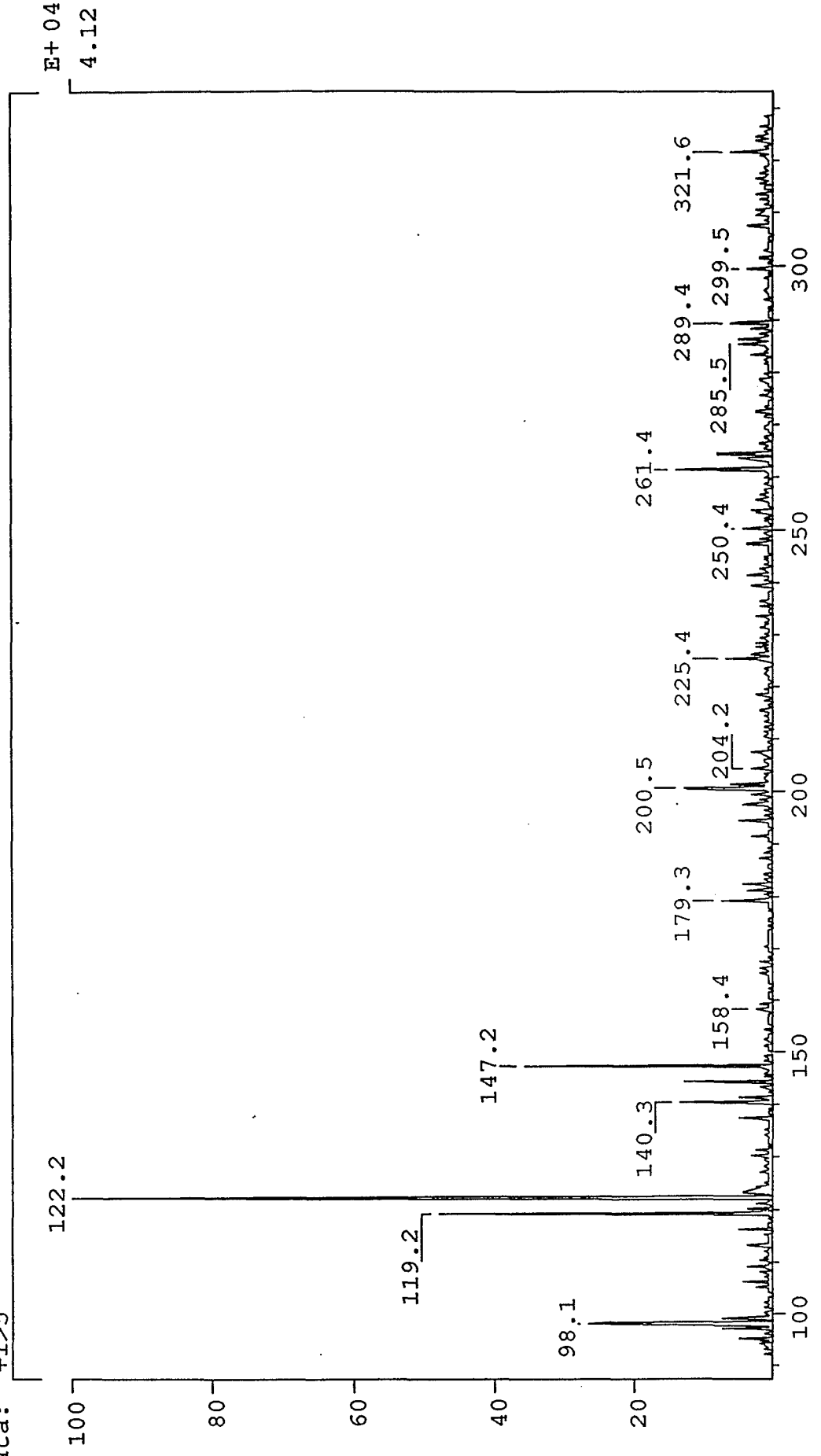
SPEC: mas793o4
 Samp: 343-1-F NG #1 treated 7-9-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: j1/hs Client: mass
 Base: 625.6 Inten : 921250
 Norm: 62.0 RIC : 11675000
 Peak: 10.00 mmu
 Data: +1>5

DERIVED SPECTRUM 9
 Start : 11
 Study : water samples
 Inlet :
 Masses: 38 > 633
 #peaks: 4180



SPEC: mas793o4
 Samp: 343-1-F NG #1 treated 7-9-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -LMR BSCAN UP PROF
 Oper: jl/hs Client: mass
 Base: 625.6 Inten: 921250
 Norm: 122.2 RIC : 11675000
 Peak: 10.00 mmu
 Data: +1>5

DERIVED SPECTRUM 9
 Start : 11
 Study : water samples
 Inlet :
 Masses: 38 > 633
 #peaks: 4180



SPEC: mas793o2
 Samp: 343-3-F PGDN treated 7-12-93
 Comm: Neg - ESI, 1.2ul flow, 1.2ul IPA sheath
 Mode: ESI -VE -IMR BSCAN UP PROF
 Oper: j1/hs Client: mass
 Base: 62.1 Inten: 3119500
 Norm: 62.1 RIC: 65561750
 Peak: 10.00 mmu
 Data: +1>7

28-Jul-93

DERIVED SPECTRUM
 Start: 15:40:27
 Study: water samples
 Inlet:
 Masses: 38 > 633
 #peaks: 12784

9
12

